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SPECIAL FOCUS: REFINING TECHNOLOGY

- 17 **HPNA woes—A thing of the past**
S. Singh, I. Clarke and E. R. Önder
- 31 **Asphaltene removal technology produces novel cement waterproofing additive**
W. Chung, M.-T. Lee, C.-Y. Chen, F.-P. Chen and T.-B. Lin
- 35 **Enterprise-wide energy efficiency fleet monitoring tool**
K. Trivedi, S. Nehete and J. Gunter
- 41 **Enhanced unit monitoring enabled by digital twin**
J. Chellani, G. Winter and A. Alshaikh
- 47 **Improve kerosene mercaptan sweetening with fluoropolymer-cartridge liquid-liquid coalescers**
T. H. Wines, A. Gorin, J. Rios and J. Trucko

CATALYSTS

- 55 **Deliver high levels of SO_x reduction with SO_x-reduction additive**
C. Baillie and C. Cooper
- 59 **Avoid common pitfalls in upscaling catalytic fixed-bed reactors**
B. Sungnoen, W. Tanthapanichakoon and K. Lourvanij

PROCESS OPTIMIZATION

- 65 **Management of LPG pool in a complex refinery**
A. Saka and D. Kutman
- 71 **External pressure design of large-diameter piping: Optimal analysis approach**
S. Maiti
- 75 **Implementation of advanced level control techniques in refinery operations**
K. K. Mandal

MAINTENANCE AND RELIABILITY

- 79 **Corrosion under insulation on stainless steel**
S. Rupesh

PROCESS CONTROLS, INSTRUMENTATION AND AUTOMATION

- 81 **Monitor ppb monomer impurities and catalyst poisons with process GC-MS**
J. Wasson and T. Russell

DEPARTMENTS

- 4 Industry Perspectives
- 8 Business Trends
- 85 Innovations
- 88 Show Preview
- 89 Advertiser Index
- 90 Events

COLUMNS

- 7 **Editorial Comment**
Refining's evolution:
Technology driving innovation
- 13 **Reliability**
Calculating the value of upgrading:
Shortcut estimations find savings
and payback

WEB EXCLUSIVE

People

Cover Image: A view of KT - Kinetics Technology's delayed coking unit at the 350,000-tpy LOTOS ASFALT Z.O.O. facility in Gdansk, Poland.
Photo courtesy of Maire Tecnimont.

HP Awards finalists: Honoring the best of the industry

In mid-August, *Hydrocarbon Processing* announced the finalists of the 2021 HP Awards, celebrating innovative technologies and people that have been instrumental in improving facility operations over the past year and are making the HPI safer, more efficient and more profitable. These people and companies deserve recognition for their achievements; the HP Awards was established to do just that.

The 2021 HP Awards cover 18 strategic categories in the HPI. More than 100 nominations were submitted for this year's awards. Each abstract was voted on by an independent *Hydrocarbon Processing* advisory board. The following is a complete list of all categories to be honored at the virtual awards ceremony, which will be streamed around the world on October 28.

The list of award categories includes:

- Best AR/VR/AI Technology
- Best Asset Monitoring Technology
- Best Automation Technology
- Best Catalyst Technology
- Consulting Firm of the Year
- Best Cybersecurity Program/Software
- Best Process-Plant Optimization Technology
- Best Digital Twin Technology
- Executive of the Year
- Best Gas Processing/LNG Technology
- Best Health, Safety or Environmental Contribution
- Best Modeling Technology
- Best Instrument Technology
- Most Promising Engineer
- Best Petrochemical Technology
- Best Refining Technology
- Sustainability Award
- Lifetime Achievement.

For a complete list of nominees in each category, visit www.HydrocarbonProcessing.com/awards. Each nominee and/or nominee's technology will be featured in the October issue of *Hydrocarbon Processing*. The November issue of *Hydrocarbon Processing* will detail the winners in each category.

For those that cannot wait to learn the winners of each category, *Hydrocarbon Processing* will be streaming the awards via a digital platform, as well as live tweeting during the event. This will allow downstream processing professionals around the world to follow the awards show in real time. The award winners will also be posted to the *Hydrocarbon Processing* website on Friday, October 29.

In addition to a full write-up of the nominees and winners within the November issue, *Hydrocarbon Processing* will broadcast this material through *Hydrocarbon Processing's* daily e-newsletter and all social media channels. The editors invite you to re-post, re-tweet, etc., the nominees and winners of these prestigious awards.

Hydrocarbon Processing would like to congratulate all nominees on this distinguished honor. **HP**

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Refining's evolution: Technology driving innovation

Since its inception in 1922, *Hydrocarbon Processing*—originally called *Petroleum Refiner* when first published—has focused on delivering the latest refining technologies to readers around the world. Whether it is the latest in new processing technologies, maintenance, best practices, case studies, tools and services, etc., the publication strives to provide hydrocarbon processing personnel with the knowledge and know-how to optimize safer and more efficient, profitable and sustainable operations.

Throughout the decades of publishing, trends and technologies have evolved significantly within the refining industry. Needless to say, no one could have predicted the demand destruction that entailed due to the response to the COVID-19 pandemic. Travel restrictions and lockdowns had a detrimental effect to refined fuels demand globally, forcing several refineries to close or convert to storage terminals. Forecasts show that 3 MMbpd–3.5 MMbpd of refining capacity could cease operations due to depressed margins caused by declines in refined fuels demand.

Market volatility has also led many owner-operators to rethink capital investments. Many projects have been put on hold, have delayed final investment decisions, halted construction activities due to safety concerns or even canceled/abandoned refining capacity builds. For example, the refining sector witnessed a nearly 23% decline in active projects year-over-year, according to Gulf Energy Information's Global Energy Infrastructure (GEI) database.

Not all doom and gloom. Despite the significant declines in global fuels demand, several forecasts show fuels demand increasing in the future. For example, according to the U.S. Energy Information Administration's *Short-term Energy Outlook*, August 2021, global oil consumption is forecast to average nearly

98 MMbpd in 2021 and increase to more than 101 MMbpd in 2022. In the International Energy Agency's *Oil 2021*, global oil demand is forecast to surpass 104 MMbpd by 2027. This is a stark contrast from 2020 consumption when demand fell below 85 MMbpd in April 2020. Although the refining sector has witnessed its fair share of project cancellations, the sector is forecast to add a significant amount of primary and secondary unit capacity over the next several years. According to various reports, global crude distillation capacity is forecast to increase by approximately 5 MMbpd by 2026.

Secondary unit capacity additions are forecast to be even more robust, increasing by 10 MMbpd within the same timeframe. Globally, the largest gain in secondary unit capacity will be for desulfurization capacity to curb sulfur in transportation fuels.

Technology driving innovation. Refining expansions, revamps and grassroots facilities are being built not only to produce cleaner transportation fuels but also to improve operations, safety, efficiency and profitability, while boosting energy efficiency and mitigating carbon intensity. The technologies being used to conquer these challenges are the primary focus within this issue's Special Focus section.

Conventional refining technologies continue to evolve, while energy transition technologies integrate into existing refining operations. This evolution includes the increase production of biofuels, renewable and alternative fuels, as well as the use of new digital technologies to monitor, adjust and optimize workflows, supply chains and processing units for optimal efficiency.

The industry's brightest minds continue to provide the technologies and services to ensure production targets are met and workers remain safe, while increasing margins and building sustainable operations. In essence, this is the true meaning of optimizing performance. **HP**

INSIDE THIS ISSUE

8 Business Trends.

This month's Business Trends explores the key concepts of blockchain, the use case and evidence for blockchain technology in the oil and gas industry, the current state and future of the blockchain patent landscape, and what this could mean for the sector.

13 Reliability. Bearings are precision components; to survive, they require clean lubricants in adequate amounts. Even seemingly small amounts of contamination can greatly reduce equipment reliability and uptime. Using bearing housing protector seals as a typical example, this article shows how the business case can be made for improvements.

16 Refining Technology. This month's Special Focus explores several technologies that are advancing the global refining industry. From new processing technologies to incorporating digital software/platforms into control systems, refiners around the world are investing in ways to optimize facility performance.

59 Catalysts. This month's Catalysts section explores the commercialization of a new fluid catalytic cracking additive technology for sulfur oxides reduction and best practices to avoid common pitfalls in upscaling catalytic fixed-bed reactors.

88 IRPC Operations Show Preview.

IRPC Operations will be held virtually September 21–22. This global, virtual event will feature three tracks that focus on optimizing refining and petrochemical plant operations. Nearly 70% of the event's presentations will be led by owner-operator organizations from nearly 20 countries around the world.

Patents provide a unique insight into oil and gas blockchain opportunities

Blockchain and distributed ledger technology have gained widespread media attention in recent years, with much of the spotlight falling on Bitcoin and other cryptocurrencies. Sectors beyond the crypto bubble are now recognizing the potential for positive disruption to traditional ways of working. Investment in blockchain technology within the energy sector is predicted to exceed \$5.8 B by 2025. To secure returns on their investments in the technology, blockchain developers are seeking to monopolize their technology using patent systems around the world. However, patent statistics show that blockchain developers are narrowly focussed on fighting for a stake in limited territories, which presents a window of opportunity for industries such as oil and gas that operate beyond those countries seeing the densest filing of blockchain patents.

This article explores the key concepts of blockchain, the use case and evidence for blockchain technology in the oil and gas industry, the current state and future of the blockchain patent landscape, and what this could mean for the sector.

What is blockchain? Blockchain at its core is a distributed, digital ledger. The digital ledger stores data while keeping an unalterable record of what data has been stored over time. Each block on the blockchain stores its own respective data. The type of data will be specific to what the blockchain is being used for and could include the details of a transaction or a smart contract. Each block points to the previous block by keeping a record of the previous block's ID, thereby forming the "chain." Another block is added to the chain each time new data is generated (FIG. 1).

Decentralization. The blockchain system is a peer-to-peer network that does not require a central authority to dictate and manage the digital ledger. Instead, the digital ledger is distributed amongst the system participants who manage the blockchain between themselves. To ensure that the participants are working with a common "true" digital ledger, the blockchain system operates on a consensus basis. This means that the "true" ledger will be the ledger that at least half of the participants agree upon. As such, participants can add blocks to the digital ledger, if it can be validated by the other participants. Therefore, the blockchain system encourages trust and transparency between the parties involved, without having to rely on a central authority.

Immutability and security. The various cryptographic techniques used in blockchain make it very difficult for a malicious party to tamper with the stored data. This can be appreciated with the basic understanding that the specific ID of a block is dependent on its data and the ID of the previous block

in the chain. Therefore, tampering with the data in a block will corrupt the block's ID and interrupt the natural chain. Cryptographic techniques make it impossibly slow and computationally expensive to make the chain look "whole" again. Nevertheless, the consensus model ensures that a tampered version of the digital ledger is not easily accepted by the system, which adds a further layer of security.

Another key feature of blockchain is its ability to execute smart contracts. A smart contract can be thought of as a conditional transaction that is stored on the blockchain, whereby the conditions of the transaction mimic the terms of the contract. Once the terms of the contract are met, the blockchain will automatically process the transaction by transferring funds or assets accordingly. Since there is no need for a middleman or broker, smart contracts can facilitate leaner, cheaper and faster interactions between parties.

The oil and gas sector is primed for blockchain. The oil and gas sector is built upon a sophisticated web of supply chains and distribution models criss-crossing the globe. As well-honed as these systems are, it is inevitable for various inefficiencies and expenses to be encountered along the way. The supply chains typically involve many individual entities, with each entity generating large amounts of data in carrying out their individual operations. This data can be inconsistently managed and communicated between entities, which can lead to misinformation and inefficiencies. Furthermore, entities are often placed under complicated contractual obligations because of collaboration, which can be difficult to execute.

A supply chain underpinned by blockchain offers trust, transparency and consistency in the way that data is handled and

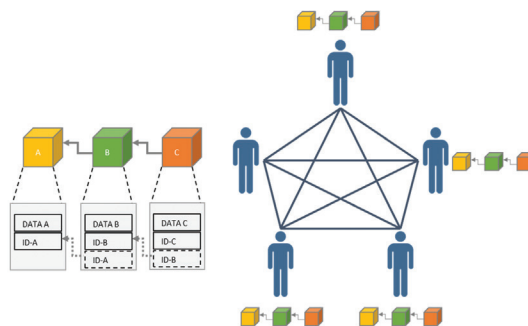


FIG. 1. The blockchain model leads to some particularly useful characteristics.

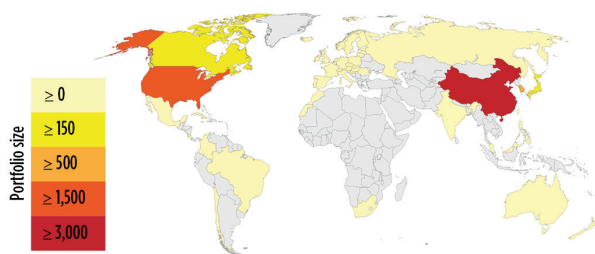


FIG. 2. Blockchain patent filings around the world.

communicated between entities. The decentralized and immutable nature of blockchain will enable entities to trust that they are using up-to-date and accurate data that is consistent with counterpart data available to the other entities. Cost-savings and improved efficiencies along supply chains should arise because the system is not hindered by the need for a central authority. Smart contracts also offer particularly special advantages with their ability to automatically execute and enforce contractual agreements in real time, saving time and money for the entities involved. Of course, some data generated by entities may be confidential, and it is well within blockchain's capability to realize what is known as a permissioned system, which can adhere to certain requirements of confidentiality between entities.

Recent years have seen mounting evidence for blockchain evolving from a disruptive technology to tangible gains in the oil and gas industry. In June 2020, the Offshore Operators Committee (OOC) Oil and Gas Blockchain Consortium released the results of a pilot blockchain platform for automating and managing water haulage from field readings to invoice payments. Initial results indicated that the traditional 90-d–120-d process was reduced to just seven days. This was achieved by reducing the number of workflow steps by more than half by removing all manual interventions. Moreover, 85% of all volume measurements were automatically validated, with the project aiming to reach 100% automatic validation in the future. Contract costs have been reduced by 25%–35% using blockchain-based smart contracts.

Also in June 2020, BHP Billiton completed its first iron ore trade on a blockchain platform, worth \$14 MM. This followed BHP's September 2019 announcement that they will start using blockchain technologies to digitize and streamline their supply chain. BHP reported that the blockchain platform was able to automatically process contractual terms, exchange digital documents between entities and provide real-time visibility of the cargo.

Blockchain adoption has been slower in the downstream processing sector; however, there has been increased activity over the past year, with major petrochemical players such as BASF and Dow publishing their own pilot programs. BASF's pilot used blockchain to track the recyclability of plastics in British Columbia, Canada, by embedding a marker into the plastic material that can survive recycling, enabling the scanning and tracking of the percentage of recycled content, the type of plastic recycled, the manufacturer and the number of times the material has been recycled. The intention is to promote an economic model in which manufacturers can generate a credit/token each time the plastic is recycled.

Dow Polyurethanes launched a pilot in early 2021 to track the compositional information of mattresses during recycling

in its Renuva mattress recycling program. In addition, cross-industry collaborations with an initial upstream focus, such as Blockchain for Energy, are now actively seeking membership across the full oil and gas value chain.

The patent landscape. The enormous potential of blockchain technology has seen early investors seeking to maintain exclusivity to maximize their returns. The most effective way of achieving this is using patent systems around the world.

Patent filing statistics show that the number of blockchain patent applications filed globally has skyrocketed since 2016. Many blockchain patents have already been granted, and the number of new applications continues to increase unabated. The largest proportion of blockchain patent applications are being filed in China, followed by the U.S. and South Korea (FIG. 2). Patents are territorial to the countries in which they are granted, which indicates that blockchain developers are most concerned with seeking exclusivity for their technology in these top countries. There is comparatively little regard for the rest of the world in the eyes of those seeking to patent blockchain technologies.

Given the relative infancy of blockchain technology, it can be expected that a fair number of blockchain patent applications may be attempts at land-grabs of key technological ideas. As such, there is a high chance of high volumes of patent litigation in the future, similar to that experienced by the telecoms industry a decade ago. This effect could be amplified for blockchain technology given its reach across many industry sectors.

If the focus is in China and the U.S., then this leaves open a wide amount of freedom and opportunity in other territories. Territories key to the oil and gas supply chain—such as Norway, the Persian Gulf region and Australia—are seeing little patenting activity for blockchain technology. Therefore, oil and gas entities operating in those territories could benefit from a natural immunity from patent holders in China and the U.S. Furthermore, this lack of activity may indicate that there is still a wealth of blockchain technology to be developed and exploited in the oil and gas industry.

Takeaway. Blockchain technology is proven to provide many benefits to the oil and gas sector. The decentralized and immutable nature of blockchain can improve trust and transparency between entities. Increased digitization and process automation will create time- and cost-savings throughout supply chains. With most patenting activity currently limited to a few specific regions, a window of opportunity has opened for sectors such as oil and gas with a wider geographical reach. It will be fascinating to see which companies exploit or monopolize blockchain over the next decade in key oil and gas regions beyond those seeing the current surge in patent filings. **HP**

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Calculating the value of upgrading: Shortcut estimations find savings and payback

Bearings are precision components; to survive, they require clean lubricants in adequate amounts. Even seemingly small amounts of contamination can greatly reduce equipment reliability and uptime. Using bearing housing protector seals as a typical example, this article shows how the business case can be made for improvements.¹

By the late 19th century, lip seals of various configurations were developed as bearing protector components. A 1940 vintage lip seal activated by a garter spring is shown above the simulated centerline in FIG. 1. However, lip seals are prone to wear and, since about 1970, have been largely superseded by modern rotating labyrinth seals. Today's advanced or "best available" models are often engineered with axially moving O-rings, and one such product is shown below the centerline in FIG. 1.

Many texts make a compelling case for preventing water intrusion into bearing housings. Once saturation is reached, the oil will absorb no additional water. Added water will exist as "free water," and bearing life will be greatly reduced. Making the business case for seals to keep out water may become necessary. Proving the value of rotating labyrinth seals is made possible by examining local maintenance records or by using shortcut-style, generally applicable "rules of thumb." These rules are readily demonstrated in a few examples.

Comparing cost of ownership. Contrasting the total cost of ownership of a set of lip seals with that of two labyrinth seals will prove revealing. Our comparison assumes a cost of \$20 for two lip seals. However, lip seals wear relatively rapidly and typically require replacement after only 2,000 operating hours. Accordingly, and in this example case, they will need to be replaced four times per year.

Comparison with a pair of rotating labyrinth seals at \$600 and, conservatively,

surviving 4 yr is rather telling. In either case, the cost of maintenance labor would be \$1,000 per event. Lip seal replacements would cost [$\$20 + \$1,000 \times 4$] = \$4,080 per year, or \$16,320 over 4 yr. Rotating labyrinth seals would cost $(\$600 + \$1,000) = \$1,600$ over a 4-yr period, or \$400/yr. Here, the true cost of lip seals would be 10 times that of modern rotating labyrinth seals!

Calculating upgrade justification. Upgrades justified by calculations based on rules of thumb use a different approach. While perhaps not as precise as the one just submitted in the lip seal vs. rotating labyrinth comparison, three rule-of-thumb calculations have proved useful in making the business case for upgrades in the past.¹

An empirical assessment, our **first rule of thumb** assumes implementation of a

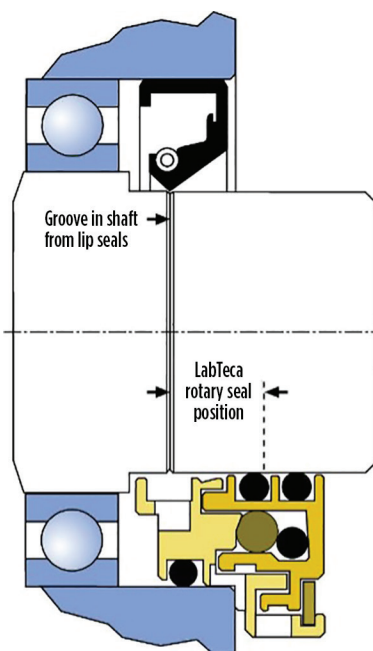


FIG. 1. Typical lip seal (top) and advanced rotating labyrinth seal (bottom). Source: AESSEAL Inc.

single upgrade measure, perhaps selecting advanced bearing protector seals. These could include the hybrid product shown in FIG. 2, or the considerably simpler product shown in FIG. 3. Both can easily extend safe operating life by factors ranging from 1.1 to 1.4. Implementing two different upgrade measures would extend safe operating life by factors from perhaps 1.5 to 2.5; with three low-cost improvement measures tending to achieve from 2.6-fold to roughly 3.3-fold operating life.

In this example case, an average pump repair costs \$12,000 and occurs every 4 yr. We take \$3,000 as the per-year repair outlay and purchase two rotating labyrinth seals for \$600, thereby avoiding one such repair. The likely payback would be $\$3,000 \div \$600 = 5$ times/yr, or approximately every 10 wk. We also could have said that repair frequencies go from one every 4 yr

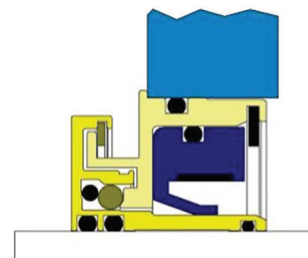


FIG. 2. Hybrid lip seal mated with advanced rotating labyrinth protector seal designed for special applications. Source: ASSEAL Inc.

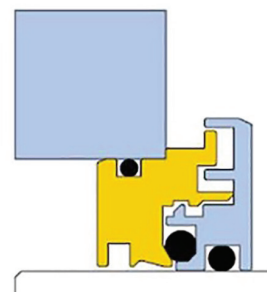


FIG. 3. A narrow-fit advanced rotating labyrinth seal. Source: AESSEAL Inc.

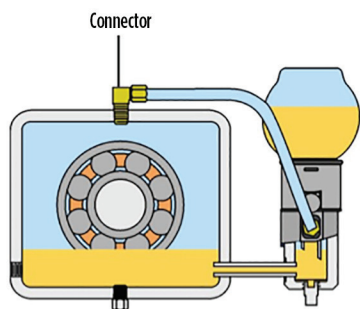


FIG. 4. Pressure-balanced constant-level lubricator. Source: TRICO Manufacturing Co.

to one every 5.5 yr. Instead of an imputed \$3,000/yr, we now only spend $\$3,000 \div 1.4 = \$2,150/\text{yr}$. We can be certain that a \$600 set of two advanced bearing protector seals will last 6 yr = \$100/yr. The payback ratio is $\$2,150 \div 100$, or about 20:1. One-twentieth of 1 yr equals about 3 wk.

A **second rule of thumb** uses an exponential approach. It assumes that if a fully upgraded machine has a reliability of 1.0, then a missed upgrade will lower the machine's reliability (or life) to 90% of $1.0 = 0.9$; two missed upgrades lower reliability to 90% of $0.9 = 0.81$; three missed upgrades to 90% of $0.81 = 0.73$; four missed upgrades to 90% of 0.73 , equaling only 0.66, and so forth. We consider this elementary rule of thumb rather optimistic; reliability or operating life expectancy with four deficiencies is probably less than 50% of what would be achieved with better bearings, better mechanical seals, better couplings or whatever other upgrades are available today.

Suppose, for example, that we had requested the purchase of a \$600 set of advanced bearing protector seals after hearing that a neighboring "Refinery X" is routinely doing this for a critical pump. We know that our critical pump has a mean time between repairs (MTBR) of 3 yr, and assume that Refinery X's MTBR reaches $3 \div 0.9 = 3.3$ yr. They, too, spend money on pump repairs. We spend $\$12,000 \div 3 = \$4,000/\text{yr}$, and "Refinery X" spends $\$12,000 \div 3.3 = \$3,600/\text{yr}$. Over a 6-yr period, we spend \$24,000; they spend \$21,600. Their \$600 upgrade returns \$2,400. Their mindset puts "Refinery X" on the track to routinely do these and similar upgrades. They either are, or likely will soon become, a best-in-class performer. Their market valuation probably tells the story of doing things smart and with forethought.

A **third rule of thumb** is also worth sharing. Again, reasonable assumptions are made; a probable 20% improvement in failure avoidance, repair cost reduction or life extension is thought to result from each upgrade. In such upgrade examinations, the first such initiative will move equipment reliability from 1.0 to 1.2, a second (different) upgrade would capture $1.2^2 = 1.44$; further upgrades yield $1.2^3 = 1.73$, and $1.2^4 = 2.07$. The implementation of four proven upgrade measures would cause the MTBR to be extended two-fold. Yearly repair expenditures would be 50% of what they were before; employees previously involved in repairs would spend time on repair avoidance tasks. Safety would go up and community goodwill would be given a boost, as would worker morale.

Using pressure-balanced constant-level lubricators. In this example, we opt for routine upgrades by (a) using sets of advanced bearing protector seals (\$600), (b) switching to extended-life synthetic lubricants (incremental cost of \$200 per charge), (c) installing pressure-balanced constant level lubricators (**FIG. 4**) (incremental cost of \$100) and (d) purpose-designed stress-relieved (annealed before final machining) brass or bronze oil rings (\$200). It would be reasonable to assume that the four upgrades totaling \$1,000 will shift the asset's operating life from 3 yr to $3 \times 2.07 = 6.2$ yr.

Suppose that our records showed it costs \$18,000 to repair the process pump in this example, and repairs would be made every 3 yr. Distributing \$18,000 over 3 yr equals $\$18,000 \div 3 = \$6,000/\text{yr}$. A one-time expenditure of \$1,100 results in spending only $\$18,000 \div 6.2 = 2,900/\text{yr}$. Prorated savings are about \$3,100 during each of the next 6 yr. Near-term payback time will be $\$1,100 \div \$2,900$, which is less than 5 mos.

Where contaminants originate. Let us return to our bearing protector seals and an examination of where contaminants originate. Moisture and dust often enter bearing housings through old-style, ineffective labyrinth seals or worn lip seals. Moisture is airborne water vapor; it could also be a stream of water from hose-down operations. Contaminants frequently enter through a breather vent, or from the widely used non-pressure-balanced

constant-level lubricators depicted in just about every pump text in print today.^{1,2} These references describe how abraded oil ring material becomes an often-overlooked source of oil contamination.

How to stop the contamination. There should be no communication or connection between the housing interior and the surrounding ambient air. Breather vents normally supplied at the top of bearing housings should be discarded and the threaded port fitted with the connector shown in **FIG. 4**. Note that the traditional open-to-surrounding-air constant-level lubricator has been upgraded to the balanced lubricator shown in this image.

Surprisingly, even the pressure-balanced lubricator in **FIG. 4** suffers from a seldom-recognized water intrusion path: the caulking that bonds the oil-filled glass bulb to its support casting. Sooner or later, caulking will develop tiny fissures or cracks, allowing water to enter through capillary action. This makes a compelling case in favor of oil mist.

The use of a face seal, along with recommendations such as deleting the breather vent and using balanced constant-level lubricators or upgrading to oil mist² will prevent the entry of virtually all external contamination into the housing. However, none of these measures will avoid contamination from inadequate oil rings and potential defects introduced by an old-style bearing housing protector seal. **HP**

LITERATURE CITED

- ¹ Bloch, H. P., *Fluid Machinery: Life Extension of Pumps, Gas Compressors and Drivers*, DeGruyter, Berlin, Germany, 2020.
- ² Bloch, H. P., *Optimized Equipment Lubrication: Conventional Lube, Oil Mist Technology and Full Standstill Protection*, DeGruyter, Berlin, Germany, To be published December 2021.



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HPNA woes—A thing of the past

2020 can be viewed as one of the most challenging periods in the history of the oil and gas sector. Unprecedented quarantines and lockdowns imposed due to the COVID-19 pandemic had a dwindling effect on fuel demand and oil prices. Refineries across the world were either shut down or had to operate at their turndown capacities. These unforeseen developments exerted significant pressure on refining volumes and margins, forcing refiners to improvise continuously to survive in this challenging market.

Hydrocracking units play an important role in converting the bottom of the barrel, waste streams and renewable feedstocks into high-value fuels, lubricants and chemicals to boost the value of refinery product slate. However, without adequate means of managing heavy polynuclear aromatics (HPNAs), most operators would struggle to process these challenging refractory feedstocks, especially in high-conversion units.

Adapting to cyclical market demands, new product specifications and increasingly stringent environment regulations are nothing new for refiners, but they now need to act swiftly and conduct thorough evaluations of their assets to remain competitive.

Refiners are increasingly processing heavier feeds, such as heavy coker gasoil, heavy vacuum gasoil and deasphalted oil, in their hydrocracker units. This is due to the industry trend for increased fuel oil conversion, particularly since the rollout of the latest International Maritime Organization (IMO) regulations. However, these factors can cause a host of operational issues, such as fouling of both equipment and catalysts that can curtail the cycle length.

The authors' company has been successfully tackling these reliability issues and offers proven catalytic and equipment solutions that ensure uninterrupted cycle

runs. Each solution is tailored around the unique features of unit configuration to harness its full potential. This proven approach reduces both the revamp scope and duration that, in most cases, ensures a swift budgetary approval and unit turnaround to implement revamp modifications. Timely commissioning of revamp is critical to the success of these projects and puts refiners in a unique position to make the most from evolving market needs.

HPNA formation, challenges and mitigation options. Straight-run vacuum gasoil (VGO) feeds naturally contain 2–6 ringed polynuclear aromatic (PNA) compounds. The concentration of these PNAs—and, therefore, their tendency to form HPNAs—increases with the increase in the VGO end point and type. For example, the HPNA formation potential of straight-run HVGO with an end point of 600°C is significantly lower compared to heavy coker gasoil or any other residue processed stream with the same end point.

As the feed passes through the hydrocracking reactors, a combination of condensation and side-chain cyclization reactions form HPNAs. These compounds, formed by undesired side reactions, are stable and virtually impossible to crack. HPNAs are fused polycyclic aromatic compounds with more than seven rings [e.g., coronenes ($C_{24}H_{12}$) and ovalenes ($C_{32}H_{14}$)]. The rate of HPNA formation increases at low hydrogen partial pressures, high conversion and at high temperatures, with the bulk of these compounds ending up in the recycle oil due to their high boiling points. HPNA build-up affects both the unit performance and reliability. Some of the key detrimental effects include:

- Hydrogen-deficient, high-molecular weight species increase the rate of coke formation, which deactivates the catalyst

and shortens the cycle length.

HPNA formation will depend on several factors (hydrogen partial pressure, catalyst type, etc.) but experience suggests that the rate of deactivation increases exponentially as coronenes in recycle oil reaches 1,000 ppm.

- As concentration of HPNAs and other difficult-to-crack compounds build up in recycle oil, reactor temperatures are raised further to achieve the target conversion. The increase in reactor temperatures often shifts the selectivity towards lighter products, leading to a decline in valuable product yields.
- HPNA buildup increases the risk of fouling in heat exchangers, leading to increased heater duty and high pressure drop across the reactor circuit. As the reactor effluent cools, HPNAs drop out of the solution due to their limited solubility and deposit in the colder exchangers in the reactor effluent train—particularly in the air cooler and cold separators—causing plugging of tubes and coalescer pads. As their concentration increases, they will also begin to deposit in warmer upstream exchangers. In some instances, plugging in unconverted oil (UCO) rundown circuits has also been reported, either due to excessive cooling or high HPNA concentration. Once this happens, it becomes virtually impossible to convert or remove these HPNA deposits online, eventually leading to unplanned unit shutdown.

A change in UCO color is usually one of the first signs of HPNA build-up. The color changes progressively from white to yellow, then to orange and red as the HPNA concentration increases. **FIG. 1**

highlights the key areas of concern as HPNAs build up in the unit.

To address the fouling concerns, almost all high-conversion hydrocrackers are now designed with a hot high-pressure separator (HHPS) at a point between the last cracking reactor outlet and the cold high-pressure separator. An HHPS typically operates in a temperature range of 260°C (500°F)–315°C (600°F), which is sufficiently high to keep the HPNAs in liquid stream that bypasses the colder sections of effluent heat exchange and prevent solid precipitation. While the hot separator design element prevents exchanger fouling, HPNAs are still present in the UCO and will build up in the recycle stream, causing significant catalyst deactivation.

It is still necessary to physically remove the HPNAs from the hydrocracker; this is usually accomplished by removing a small portion of the UCO as a purge stream. The bleed stream from the hydrocracker can range anywhere from 3%–10%. If a refinery does not have a fuel oil system or a fluid catalytic cracking unit (FCCU), this option can lead to indirect recycling of HPNAs, further compounding the issues. It also offers limited flexibility to withstand changes in feed quality and catalyst aging with time.

Often, HPNA formation increases ex-

ponentially and refiners are forced to increase the UCO bleed rate to sustain the unit operation. The resultant decrease in conversion and middle distillate (MD) yields can cost a refiner with an average size HCU (50,000 bpd or 8,000 m³/d) more than \$10 MM/yr of lost product opportunity. **FIG. 2** shows a typical conversion vs. HPNA trend for units without any active HPNA management.

Over the years, the authors' company has developed several approaches to effectively manage and limit the HPNA formation in hydrocracker units. These include both improvements to catalyst systems for better HPNA conversion, as well as new equipment innovations to aid in HPNA removal. Catalytic solutions mainly focus on saturating the starting blocks of HPNA, i.e., feed refractory species or PNAs to prevent sedimentation in both reactor and product sections. This is particularly a concern in high-conversion recycle units processing VGO with a high end point (> 600°C) and feed blends comprised of thermally cracked gasoil streams from coker, visbreaker, and FCC units and other residue derived feedstocks. The inclusion of proprietary high-activity and deep hydrogenation catalysts^{a,b,c} can help mitigate associated processing challenges with these difficult feedstocks.

Catalytic solutions. The authors' company brings a unified approach to cater to diverse hydroprocessing configurations and technologies offering a vast choice of solutions for both hydrotreating and hydrocracking catalysts. The company's hydroprocessing catalyst portfolio^d comprises of large variety of catalysts specifically designed to meet diverse and unique refiner needs around the globe. A wide range of commercially proven catalysts and technical support throughout the catalyst cycle help operators to continuously optimize unit performance, improve reliability and meet challenging market needs. For units struggling with HPNA issues, an ideal combination is usually a high-activity pretreat catalyst with a high-saturation cracking catalyst.

The use of advanced analytical techniques like a Titan 80-300 keV Super-X aberration-corrected electron microscope allows the company's scientists to better understand interactions between the active metal and the catalyst support. These and other characterization techniques have proved to be a game-changer and helped the authors' company to swiftly commercialize catalysts^{e,f} specifically designed to deliver improved hydrogenation. The company's catalysts can be used alone or stacked together depending on the unit configuration, operating conditions and cycle length. These catalysts offer excellent hydrogenation that can either be utilized for converting or saturating HPNAs or for boosting UCO VI for lube oil production. Catalyst activity is ideally suited for maximum distillate production in both single- and two-stage units.

Similarly, proprietary high-activity treating catalysts^{g,h} with enhanced metal formulation and support have proven experience in handling heavy refractory feeds. These catalysts offer high start-of-run (SOR) activity that is suited to saturate PNA, and excellent stability that delays the approach to aromatic saturation equilibrium and allows consistent operation at low nitrogen slips, all of which drastically reduce the HPNA make.

A novel unsupported catalyst^c delivers step out performance especially for refiners struggling with catalyst bed volume limitations. An advanced characterization of feedstocks and products is applied to elucidate the catalysis kinetics and determine the most suitable location for the catalyst layer(s)^c in the right quan-

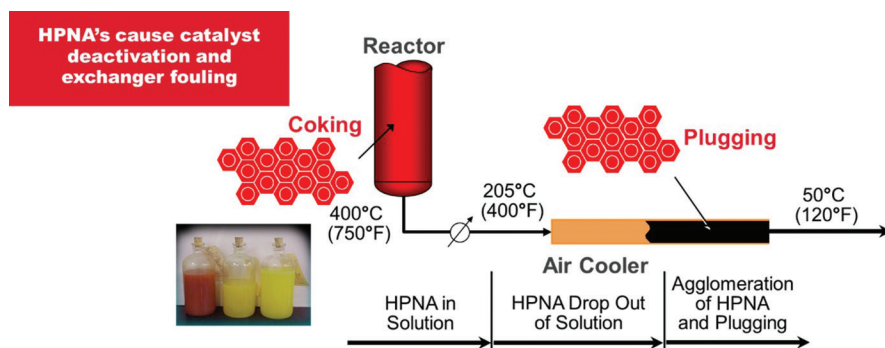


FIG. 1. Effects of HPNA buildup.

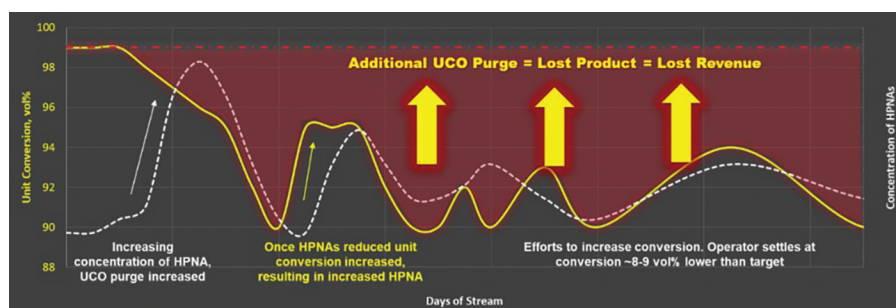


FIG. 2. Typical unit conversion trend to limit HPNA buildup.

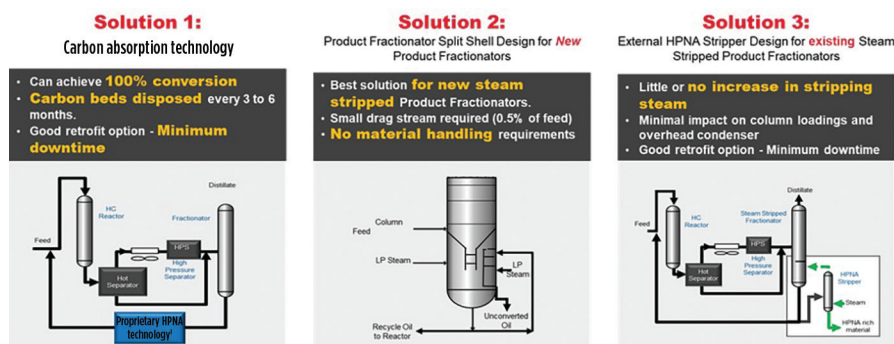


FIG. 3. Authors' company's HPNA separation equipment options.

tity. Performance testing results indicate increased hydrotreating activity in terms of both hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) mainly due to saturation of the least reactive species like dimethyldibenzothiophenes and dimethylcarbazoles. Resultant activity improvements translate to reduced bed volumes, thereby saving the undesired capital expenditure associated with new reactor installation to meet the elevated severity at low SOR temperatures.

In commercial applications, the novel unsupported catalyst^c is loaded in combination with conventional, high-performance catalysts^{b,h} to debottleneck activity, and improve reliability and product quality constraints.

Equipment solutions. While the catalytic solutions described here can help reduce the HPNA make, this is not enough to guarantee a constant low HPNA make throughout the catalyst cycle. Irrespective of the unit configuration, fluctuations in unit feed quality and the gradual fouling of catalyst hydrogenation function impact the ability of even the best hydrogenation catalysts to maintain a UCO HPNA concentration that is steady and within limits.

The exact timing and concentration at which HPNAs begin affecting unit performance may vary, but the associated economic losses are not trivial to justify living with them. Including an equipment solution, therefore, becomes imperative to overcome HPNA woes and allow the processing of opportunity feedstocks without having to bother about product yields and cycle length.

The authors' company has commercial-proven equipment solutions for HPNA separation and removal that caters to the diverse needs of both new and existing unit designs. These options can be either com-

bined with the catalytic solutions or implemented alone as part of revamp to cost-effectively mitigate HPNA reliability issues.

Solution 1 of FIG. 3 shows a recycle oil management systemⁱ that utilizes activated carbon beds to adsorb HPNAs. It comprises of two single-bed vessels that operate as lead and lag beds with the flexibility to isolate and change the adsorbent bed as it gets saturated. The lead bed becomes the lag bed following the change out. The frequency of change out can vary from 6 mos–1 yr, depending on unit operating severity and catalyst system. This option offers a simplistic design that can be conveniently incorporated into the existing unit flow scheme with minimum downtime. This technologyⁱ was commercialized in 1990 and has more than 10 units successfully operating across the globe.

A product fractionator split-shell design (Solution 2) is considered the best option for new units where the main fractionator can be built with a split-shell to include the HPNA removal section within the same column. This patented fractionation scheme utilizes high boiling point of HPNA species, especially with > 11 rings to achieve the desired separation. All HPNAs get concentrated in the UCO with a purge rate as low as 0.5% of the fresh feed rate, thereby significantly reducing the HPNA content in recycle oil to the reactors. It requires no material handling and has a minimal footprint. Since its commercialization in 2008, more than 15 units with split-shell fractionator design for both single-stage and two-stage configurations have been licensed, with multiple in commercial operation.

The external HPNA stripper design (Solution 3) utilizes the same fractionation concept but employs a small external stripper connected to the main column instead. A small slip stream from the frac-

tionator bottoms pump is routed to the HPNA stripper, where the target HPNA separation is achieved using superheated steam. Stripper overhead is routed to the main fractionator column to provide the necessary stripping, while the concentrated HPNA stream is withdrawn from the stripper bottoms.

The external HPNA stripper design is a good retrofit option with minimum changes to product fractionator operating conditions and design. Only a few pieces of new equipment, all of which are relatively small, makes this an ideal option for a modular offering. This further reduces the footprint, unit downtime and refiners work scope. The first unit was sold in 2016 and was commercialized in 2020. First-hand commissioning experience and the commercial performance details are covered in the subsequent case study.

With either solution, the refiner benefits from being able to maintain very high conversion throughout the catalyst cycle, maximizing carbon management. All equipment options offer significant economic incentives primarily due to a boost in middle distillate product yields, reduced unit conversion and the flexibility to process VGO with high end point. In most instances, these revamp options offer a very high return on investment (ROI), with a typical payback time of less than 1 yr for an average size HCU (50,000 bpd or 8,000 m³/d).

COMPREHENSIVE HPNA MITIGATIONS SOLUTIONS: A CASE STUDY

In response to the changing refining landscape, TÜPRAŞ (Türkiye Petrol Rafinerileri) was one of the few refiners in the European region that began evaluating the impact of IMO regulations on refinery profitability as early as 2009. Turkey relies heavily on imports for almost all its energy and fuel needs, as it lacks any hydrocarbons production facilities. It has a surplus of gasoline but is heavily dependent on diesel imports.

TÜPRAŞ could see the silver lining quite early and acted swiftly to upgrade the refinery configuration and take advantage of the declining fuel oil market. The shift in market dynamics provided a perfect opportunity to leverage the difference in fuel oil and diesel prices to justify the Residuum Upgrade Project (RUP), which aimed



FIG. 4. (Left) Location of Tüpraş' refineries, Turkey; (right) Aerial view of the RUP complex, Izmit refinery.

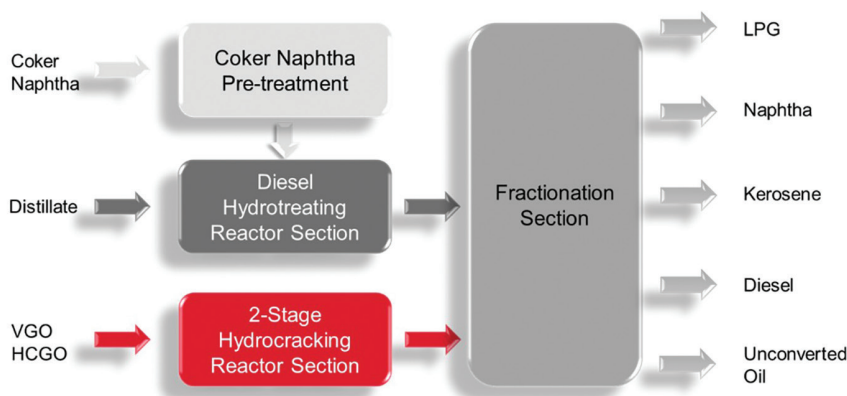


FIG. 5. Integrated RUP hydroprocessing units flow schematic.

to increase the flexibility of the Izmit refinery (one of four Tüpraş refineries) to process heavier and high-sulfur crude oils, together with the capability to convert 4.2 MMtpy of high-sulfur fuel oil to 3.5 MMtpy of valuable high-quality white products, such as diesel, jet fuel, gasoline and LPG conforming to Euro-5 specifications.

Based on its internal evaluation, Tüpraş had clear aspirations to reduce its fuel oil production and chose one of the most common and proven refinery configurations for residue conversion: a delayed coking unit (DCU) with downstream hydrocracking and hydrotreating units for upgrading all coker products. This widely used option offers a reliable configuration with minimal risk at the lowest capital cost. However, the biggest challenge was to create an integrated hydroprocessing complex design that offered the desired degree of flexibility between the hydrocracking and hydrotreating units at optimum CAPEX and OPEX costs to keep the project economically viable.

Tailored integrated design. The authors' company developed several potential configurations and analyzed the pros and cons to help Tüpraş choose the most optimum solution. Each poten-

tial configuration included an analysis of resources requirements for both people and equipment, high-level performance projections, cost estimates and constructability rankings. This iterative process enabled the Tüpraş team to refine objectives, understand the numbers in detail and provide feed definitions to optimize the cut point between straight-run VGO and coker feed to optimize unit sizes. The collaboration ultimately resulted in an ideal configuration to meet the project objectives. **FIG. 4** shows the refinery location (left) and an aerial view (right) of the site.

The selected design comprised of an integrated coker naphtha and distillate process unit^l, with all product rundowns routed to a process unit fractionation section^k. Key common high-pressure equipment, such as washwater pumps, make-up gas compressors and amine pumps, helped improve the integration and reduce costs without compromising the degree of flexibility. Extensive heat recovery between the units and common PSA for recovery of CLPS off-gases from the complex helped minimize the carbon footprint.

For the hydrocracking unit configuration, Tüpraş chose a proprietary enhanced two-stage process^l to minimize the impact of difficult feeds on the product

yields. The unique flow scheme and the tailored catalyst system offered high middle distillate yields, while reducing energy, hydrogen consumption and other costs compared with competing technologies. A high-level flow scheme of the integrated hydroprocessing units is shown in **FIG. 5**.

The RUP complex comprised the following main units: vacuum unit, delayed coker, integrated hydrocracker and hydrotreating units, hydrogen generation unit, two trains of sulfur recovery units, an amine regeneration and a sour water stripper unit as well as a new cogeneration unit (120 MW). The project was completed in ~4 yr at an estimated cost of \$3.2 B, including utilities and tank farm area. All units were successfully commissioned by 3Q 2015.

The 50,000-bpd (8,000-m³/d) unit^k was designed to process a 60:40 feed blend of HVGO/HCGO at 98 wt% conversion. An integrated hydroprocessing complex checkout was begun in July 2014 and the units were successfully commissioned in May 2015. A demonstration test run confirmed that the units are meeting or exceeding performance guarantees.

Technical support. The original unit design solely relied on the UCO purge and a customized catalyst system to prevent the HPNA buildup. It worked well with feeds similar to the design feed case. Encouraging test run results coupled with spare margin in unit hydraulics and hydrogen availability offered further potential to increase ROI. Within 4 mos of commissioning, capacity was gradually increased to 110% of design in continuous collaboration with the authors' company's technology services to harness the full potential of the unit. Catalyst performance, key unit variables and the health of key equipment were closely monitored to stay within the design limits. Changes to feed blend, both in terms of cracked to straight-run ratio and increase in HVGO/HCGO end points, were necessary to allow Tüpraş to push the feed rate further and reduce the reliance on imported HVGO. Sustained operation at high capacity coupled with the processing of relatively heavier feed blends eventually increased the operating severity to a point where the design UCO bleed rate was no longer enough to purge the HPNAs from the system. UCO color turned from off-white to orange in a matter of days following the increase in HCGO end point by ~45°C.

Feed Properties	Design Feed		Actual Feed	
	HVGO	HCGO	HVGO	HCGO
Cracked/SR Feed ratio	0.66		0.24	
SIMDIST EP °C*	618	543	653	585
Arsenic, wt ppb	--	--	60	80
C ₇ Insolubles, Wt-%	--	--	0.03	0.06

Economic Drivers:

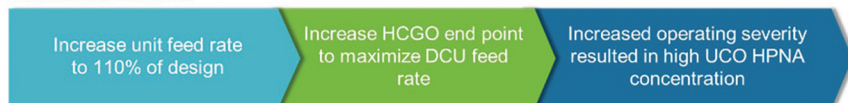


FIG. 6. Actual vs. design feed properties.

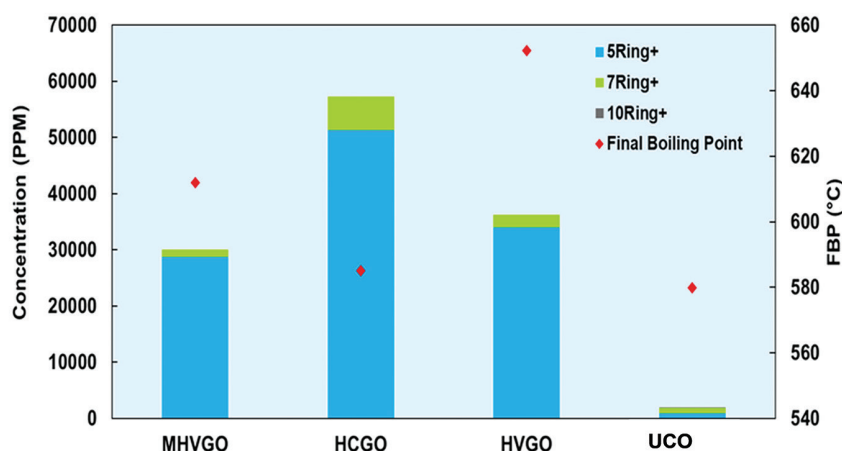


FIG. 7. HPNA break-up for different feed types.

Reducing the feed end point and conversion helped improve the situation but was obviously not the most optimum solution. Processing heavier feeds was essential to sustain the unit operation at 110% of design, but not at the cost of unit reliability and cycle length. The company performed several yield estimates at different conversion levels and feed rates for the revised feed definition. Each estimate included details on catalyst deactivation rates, products yield slate and UCO purge rate to develop a risk vs. profit metrics to help TÜPRAŞ make an informed decision. Eventually, operating the unit^k at 110% design capacity at a slightly lower conversion (~95 wt%) was selected as the most cost-effective short-term solution. FIG. 6 shows the key differences between the design and actual feed properties at high capacity.

The next step was to devise a robust feed monitoring system to effectively analyze and limit the contaminants in the feed blend and UCO. Tracking these refractory and unusual species in thermally

cracked feedstocks like HCGO is often a challenge, and bulk properties analysis is simply not enough. Over the years, the authors' company has developed a number of analytical techniques for obtaining a detailed molecular compositional analysis of extremely complex heavy streams. These analyses identify feedstock compounds that are known to be precursors of catalyst coke and of 11+ ring HPNAs.

The two most frequently used and reliable analyses are high-performance liquid chromatography (HPLC) and fluorescence spectroscopy (FS). The HPLC test method harvests and quantifies the refractory species—especially pure ovalenes and coronenes—in both feeds and UCO, while FS reports HPNA types as a function of different wavelengths at which peak fluorescence intensity occurs. The higher the wavelength, the greater the number of rings. FS is usually the preferred test method for tracking HPNAs with 11+ rings.

The authors' company provided the necessary training, lab equipment specifications and test methods to help TÜPRAŞ

set up an in-house capability to perform quick analysis and make necessary adjustments to prevent HPNA buildup. Another change was to replace the ASTM D1160 distillation test method with SIMDIST D7169 to better control the feed tail end and minimize residue entrainment.

Simultaneously, process unit^k feed and UCO samples were shipped to the authors' company's laboratories to develop a better understanding of the feed recalcitrant species using advanced characterization techniques. Detailed compositional analysis of these hydrocracker streams was then used to estimate the difficulty of feedstock processability using the authors' company's correlations to both develop catalytic solution for the next cycle and to optimize the unit operation for the existing cycle.

FIG. 7 shows how advanced characterization methods like high-resolution mass spectroscopy (HRMS) can be utilized to optimize unit operations by identifying the feed contaminants at a molecular level and reduce the potential for rapid catalyst deactivation. The four bars indicate the PNA/HPNA breakup by ring numbers. Red dots are the distillation end point of each of the feed blend components. The relative concentration of 5 and 7+ ring compounds or PNA precursors is much higher in HCGO, even though its end point is lower than the straight-run VGO.

An increased proportion of these precursors in the feed eventually results in HPNA buildup in the unit at high conversion. These analyses were consistent with the authors' company's recommendations to either control the HCGO end point to operate the unit at design conversion or reduce the unit conversion to address HPNA buildup issues. It also serves as a reminder that feed bulk properties like distillation, API, etc., are insufficient to predict the HPNA precursors, particularly in thermally cracked feedstocks. Advanced feed characterization and improved in-house feed and UCO monitoring helped improved the unit reliability and achieve the guaranteed cycle. FIG. 8 shows the impact of HPNA buildup on unit conversion.

Addressing HPNA woes. The first catalyst cycle clearly exposed the vulnerabilities of high-conversion units without any active HPNA management solution to changes in the feed slate. Costs associated with reduction in MD yields and shorter cycle length were simply too high to justify

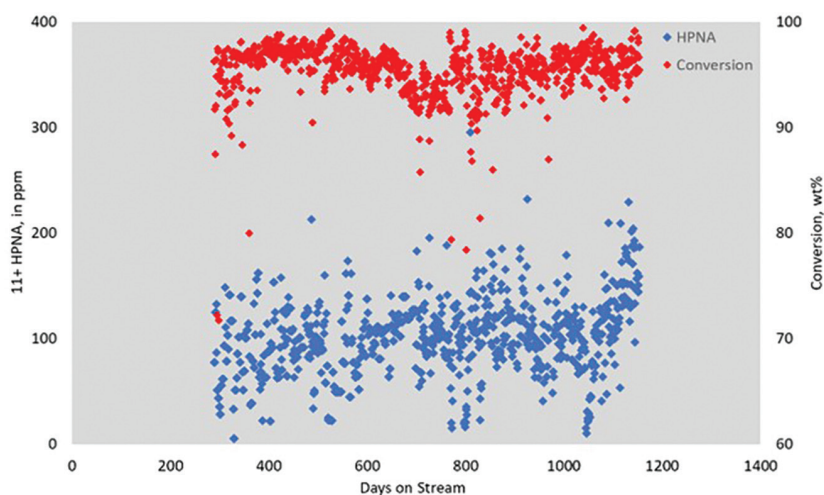


FIG. 8. Plot showing impact of HPNAs on unit conversion.

living with HPNA woes for the next cycle. The authors' company continued to work closely with TÜPRAŞ to develop a comprehensive HPNA mitigation solution based on its future needs. The primary objective was to consistently push the unit operating severity by processing HS feed blends with high EP ($> 600^{\circ}\text{C}$) at 110% capacity at ≥ 98 wt% conversion. TÜPRAŞ also wanted to extend the catalyst length from 3 yr to 4 yr with > 80 wt% distillate yields without any HPNA buildup.

Equipment solution: Different HPNA options, such as an activated carbon bed chamber, split-shell fractionator and SDA on HCGO stream, were reviewed with TÜPRAŞ. In 2016, the split-shell fractionator design and carbon beds for HPNA absorption were fully commercialized solutions. The standalone HPNA stripper design, though commercially unproven, met TÜPRAŞ' needs and processing objectives. The risk in trying this option was low, as it was based on the split-shell fractionator working principle and offered the same separation efficiency but without any major modifications to the existing equipment.

The carbon beds option was also considered but rejected due to plot constraints and the associated recurring costs of adsorbent replacement. A standalone HPNA stripper was found to be the most economically attractive option, requiring no additional unit downtime to include the new equipment with the unit flow scheme. With the installation of an HPNA stripper, TÜPRAŞ could increase the unit conversion to 99.5 wt%, while

processing high-end point ($> 600^{\circ}\text{C}$) HVGO/HCGO feed. Project work commenced in January 2016 and the basic engineering design package was delivered within a couple of months.

Catalytic solution. Maximizing the middle distillate yields and flexibility to process opportunity feedstocks without any HPNA buildup was a key requirement to improve refinery margins. TÜPRAŞ had good commercial success with the typical low-activity and high-selectivity catalyst system designed specifically for a second-stage environment. However, catalytic activity was simply not enough to guarantee a low HPNA make with constant fluctuations in feed quality throughout the cycle. The knowledge gained from the unit operation, constraints and catalysts' shortcomings were leveraged to develop a tailored catalytic solution specifically designed, keeping the following TÜPRAŞ needs in mind:

- Ability to operate the unit at 110% design feed rate, while meeting desired cycle length of 48 mos
 - Flexibility to intermittently process heavy feed blends
 - Superior hydrogenation for HPNA conversion in Stage 2 environment
 - Flexibility to shift the conversion between the two stages with minimal impact on middle distillate yields
 - Ability to operate the unit at 99.5 wt% conversion with the HPNA stripper online
 - Improved product quality throughout the catalyst lifecycle.
- High-activity treating catalyst[®] with

superior hydrogenation functionality were chosen to maximize the volume swell and HPNA conversion. A pilot plant (PP) test was performed with TÜPRAŞ feed and operating conditions to verify representations.

The process unit^k was shut down in February for a scheduled turnaround and catalyst changeout, and was reloaded with the selected catalyst system and started up in May 2019. While all the tie-in connections for the HPNA side stripper were taken during the unit turnaround, the HPNA stripper could only be commissioned in September 2020 due to delays in mechanical completion.

The new catalyst system has now been online for more than 18 mos and has successfully met or exceeded all key processing objectives. Unlike the last cycle, the unit is consistently running at 110% design capacity at or above design conversion, with significantly reduced and steady HPNA make. High second-stage SOR activity and improved hydrogenation has allowed TÜPRAŞ to regularly process heavier feed. It is also now possible to swing the conversion between the two stages and balance the catalyst deactivation rates, especially while processing difficult feeds, without impacting MD selectivity.

The first plot on the left in FIG. 9 shows consistent high distillate yields, better than the previous catalyst system. The plot on the right in FIG. 9 shows the difference between the WABT of two catalyst systems. An SOR temperature of the catalyst[®] was and continues to be about 30°C lower than the previous cycle. Improved activity has not only helped to reduce HPNA make, but offers the flexibility to regularly process heavier feeds without having to compromise on conversion.

Low SOR temperatures and higher bed exotherms in the second stage also reduced the fired heater duty by about 10%. The resultant spare margin provides further flexibility to increase the feed rate to second stage and therefore improve the middle distillate selectivity by reducing the conversion per pass, especially while processing difficult feed stocks.

Good and consistent catalyst performance prompted TÜPRAŞ to push the operating severity further both by increasing the feed end point and by increasing the HCGO in the feed blend. In the last cycle, processing such heavy feeds was unimaginable without having to reduce the

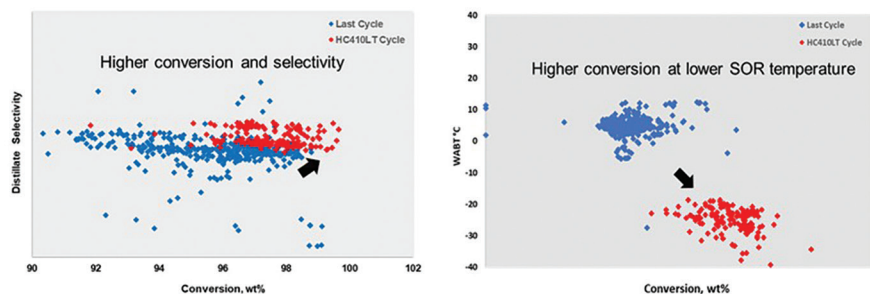


FIG. 9. (Left) Distillate selectivity cycle comparison; (right) 2nd-stage catalyst activity cycle comparison.

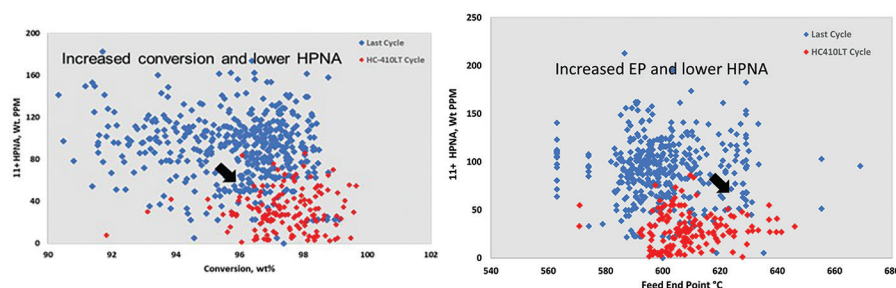


FIG. 10. (Left) HPNA make vs. feed EP comparison; (right) HPNA make vs. conversion comparison.

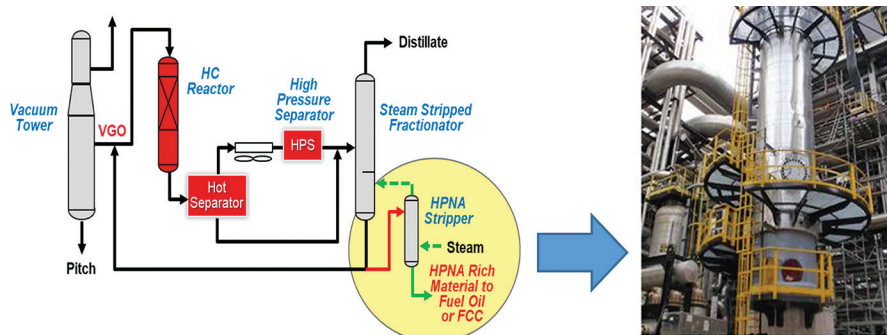


FIG. 11. (Left) Typical external HPNA stripper flow scheme; (right) HPNA stripper in operation.

unit conversion to keep recycle oil HPNAs below 200 ppm, especially at EOR conditions. This is now a thing of the past.

The plot on the left in **FIG. 10** demonstrates superior hydrogenation performance of the catalyst^e that has kept the HPNA make consistently below 50 ppm while processing feeds with an EP > 600°C. With the reduction in refinery margins and the advent of IMO regulations, the new catalyst system has helped boost the overall revenue by operating the coker unit at higher capacity and increasing the feed end point by 20°C–30°C. The plot on the right in **FIG. 10** shows the HPNA generation as a function of unit conversion. At SOR conditions, the HPNAs were in the range of 20 ppm–40 ppm at or above design conversion, as compared to 100 ppm–120 ppm HPNAs in the previous cycle.

The catalyst system^d continues to meet or exceed TÜPRAS^g goals, consistent with predicted performance. In addition to providing excellent catalyst activity and selectivity, the catalyst system has demonstrated good temperature stability and is on target to meet the desired lifecycle. These process improvements are proof of the successful application of the proprietary catalyst^e in a second-stage environment to reduce HPNA make without compromising middle distillate yields.

HPNA stripper commissioning. The majority of the equipment and piping installation work for the HPNA stripper project was performed with the unit^k on-line. All tie-in points were identified during the project stage and taken during the turnaround to enable the HPNA stripper

to go online when ready without hampering the unit^k operation. These tie-in isolations also provide the flexibility to take the HPNA stripper offline for any maintenance, if required. Key HPNA stripper facts and figures are summarized here:

- Total installed cost: ~ \$5.5 MM
- Simple design, no additional unit downtime required
- Stripper size: 2-m ID × 9.1-m T/T (designed for enhanced two-stage process^{k,l} feed rate of 9,200 m³/d)
- Increased unit conversion by ~1.5 wt%
- Reduced bleed rate by 75%
- Unlocked potential to process heavy feeds and further increase profitability.

Following the mechanical completion, the HPNA stripper was taken online in September 2020 without any product slopping. Unit commissioning was quick and easy and involved two key steps:

- Heating the steam lines and stripper using the existing silencer and jump over lines. Stripping steam to the fractionator column^k was then slowly diverted through the HPNA stripper.
- Introducing the fractionator bottoms to the HPNA stripper and increasing the stripping steam superheat to achieve the desired stripping efficiency. The overhead vapor comprising mostly of steam was routed to the main fractionator column as stripping steam, while the HPNA stripper bottom product can either be routed to the coker feed tank or coke drums.

The normal and preferred routing is to the coke drums to destroy the bulk of the HPNA and reduce any potential recycle to the unit^k.

Results and takeaway. The authors' company was able to support the startup remotely due to ongoing COVID-19 travel restrictions at that time, relying on its process monitoring software solution to remotely monitor the startup operation and provide necessary recommendations. Despite local labor constraints and limited vendor support, the startup of the stripper took just 1.5 d, and the drop-in recycle oil HPNAs were evident from the first shift. **FIG. 11** provides a high-level flow scheme of the external HPNA stripper and a site photo.

Commissioning of the stripper improved recycle oil quality further and helped raise the unit conversion to 99.5%. Steady and low recycle oil HPNA concentration keeps the catalyst deactivation rate low, providing an opportunity to either extend the cycle or process more difficult feeds. The stripper design is also energy efficient, and the bulk of the energy used for superheating the steam is offset by a reduction in the fractionator charge heater duty.

FIG. 12 shows an improvement in the recycle oil quality before and after HPNA stripper commissioning. An immediate reduction in recycle oil HPNAs can be seen following the commissioning of the HPNA stripper. However, due to some operational issues with the stripping steam electrical super heater, achieving design conditions took slightly longer than expected. The first six recycle oil analyses correspond to a heater duty of 25%–50%, which translates to about 50% of the design superheat. Despite this, it was possible to reduce the HPNAs by approximately 40%, i.e., from 140 ppm to 90 ppm. The last two analyses correspond to HPNA stripper operation at design conditions with HPNA levels at just 40 ppm. The recycle oil color changed to bright yellow during the stabilization period.

The HPNA stripper has now been online for more than 3 mos with the process unit^k consistently operating close to full

conversion with no signs of HPNA build-up. **TABLE 1** summarizes the key benefits of a comprehensive HPNA mitigation solution implemented at the TÜPRAŞ enhanced two-stage unit^l.

The external HPNA stripper commissioning at TÜPRAŞ marks the successful commercialization of this key revamp technology that is especially suited for high-conversion units processing difficult feedstocks. The tailored comprehensive solution has not only helped TÜPRAŞ achieve all its processing objectives but surpass them with continuous support from the authors' company's services. The unit is now consistently able to operate at 110% capacity while processing difficult feeds above design conversion and, more importantly, without any HPNA woes. Such HPNA management customized solutions can help refiners improve unit performance and profitability via increased conversion to high-value products, which in most cases help recover the cost of investment in a matter of months.

The pivotal role of a hydrocracking unit in a modern refinery hinges on its ability to reliably process a wide variety of feedstocks. Whether a refinery is looking for a novel catalyst solution that accounts for the complexities of a new and far-reaching goal or looking for a revamp solution to achieve specific targets, the authors' company brings a unified approach

through its vast lineup of hydroprocessing catalysts^d and many decades of experience in hydrocracking technology. **HP**

NOTES

^a Honeywell UOP's HYT-6219

^b Honeywell UOP's HYT-6319

^c Honeywell UOP's ULTIMet™

^d Honeywell UOP's Unity portfolio

^e Honeywell UOP's HC410LT

^f Honeywell UOP's HC620LT

^g Honeywell UOP's HYT-6219

^h Honeywell UOP's HYT-6319

ⁱ Honeywell UOP's HPNA RM™

^j Honeywell UOP's Unionfining™

^k Honeywell UOP's Unicracking™ Process

^l Honeywell UOP's Enhanced Two Stage (E2S) Unicracking



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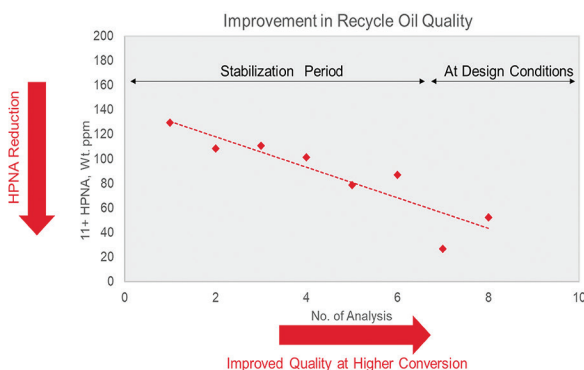


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TABLE 1. HPNA stripper performance summary

Key variables	Original design	Current cycle
Capacity of hydrocracker	Base	+10%
Cycle length	Base	+15%
HCGO end point	Base	+70°C
HVGO end Point	Base	+25°C
HPNA make	Base	-70%



HPNA Stripper at Work



FIG. 12. Improvement in recycle oil quality.

Refining Technology

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Asphaltene removal technology produces novel cement waterproofing additive

Addressing climate change and environmental issues has become a top priority in the 21st century. In recent years, global decarbonization efforts have accelerated, underpinned by civil society's demand for long-term sustainability and government mandates that set aggressive carbon emissions targets, such as net zero emissions by 2050.¹

However, despite recent advancements in the efficiency and storage of renewable energy sources (solar, wind, geothermal, etc.), petroleum is highly cost-competitive, transportable, accessible and remains a reliable medium for meeting society's short- to medium-term energy needs.

The development of new uses for refinery byproducts presents a practical solution for the pressing issues facing the downstream processing industry. Akin to the rise of petrochemicals derived from light hydrocarbons providing diversification opportunities, novel non-combustion uses for heavy hydrocarbon fractions add incremental economic value, flexibility and resilience to refinery operations. Moreover, non-combustible outlets for petroleum allow the industry to meet its environmental obligations in a green society. If left unaddressed, the regulatory costs and impairments related to lowering carbon emissions may significantly impact project economics for a refiner.

This article describes a low-cost solution for the decarbonization of petroleum while simultaneously producing byproducts that have practical benefits for other industries.

Push for decarbonization. The decarbonization movement has been spearheaded on multiple fronts, and companies with long-term, global outlooks are positioning themselves accordingly.

Between 2016 and 2017, Royal Dutch Shell, Equinor (formerly Statoil), ConocoPhillips and Marathon Oil announced the sale of the majority or all of their Canadian oil sands assets, with some also tying executive compensation to emissions cuts.²⁻⁵ In 2019, Norway's \$1-T sovereign wealth fund announced plans to divest from oil and gas exploration and production companies.⁶

Conversely, companies with exposure to heavy and extra-heavy oil assets have embraced the role of new technologies for reducing emissions. Extensive progress has been made with regard to the development and commercialization of novel methods for effectively and efficiently processing heavy feedstocks into value-added products.

Advances in residue processing. The selective extraction of asphaltenes (FIG. 1), using a proprietary process^a to cleanly and uniquely remove asphaltenes as dry virgin granules from heavy crude oil and petroleum residue, has emerged as a solution for adding cost-effective flexibility for refiners looking to maximize value from bottom-of-the-barrel streams.⁷ Upon removal of the asphaltene portion, the process^a produces a high yield of deasphalted, decontaminated and decarbonized oil suitable for conventional packed-bed hydroprocessing.⁸

The process^a is a supercritical solvent extraction technology based on the combination of an anti-solvent with multicomponent phase equilibria, and is analogous to the decaffeination process used in the food processing industry.⁹ The supercritical or near-critical solvent used in the process^a exhibits key favorable characteristics for separating asphaltenes from residue:

- Unique solvent behavior, vapor density and diffusivity, which enhance asphalt phase separation
- Facilitated turbulent mixing of petroleum feedstock and solvent, which enhances mass transfer.

The process^a has several advantages over conventional solvent extraction processes, including a smaller and simpler extractor design, higher energy efficiency, lower solvent-to-oil ratio, and deeper and cleaner separation.⁹

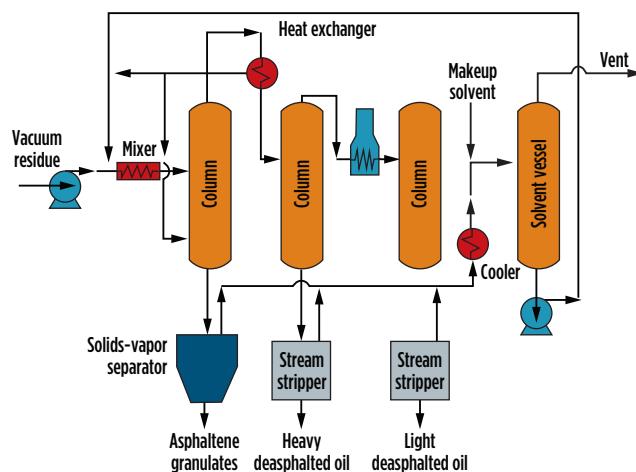


FIG. 1. Proprietary process^a flow diagram for selective extraction of asphaltenes from heavy crude oil and petroleum residues.

To date, five commercial units with a combined processing capacity of 36,500 bpd have been built in Asia-Pacific, the largest of which has a 20,000-bpd capacity. Commercial operators utilize the technology for a variety of purposes, including transforming residues into hydrotreating feedstock for the production of low-sulfur fuels, as well as for processing FCC slurry oils for the production of needle coke.¹⁰

Rethinking asphaltene processing. Traditional bottom-of-the-barrel processing techniques utilize capital and energy-intensive thermal or catalytic processes to transform carbon-intensive asphaltenes into combustion fuels; however, these methods are becoming increasingly obsolete in the context of a decarbonized and low-cost society. Through the coking process, for example, asphaltenes are transformed into petroleum coke, and are either disposed at a cost to the refiner or sold as a low-value combustion fuel in jurisdictions with eased emissions allowances. Comprising up to 85% carbon, asphaltenes are the only refractory oil constituent to refinery processing, and if ultimately used for combustion purposes, their emissions intensity is comparable to that of coal.

The novelty of the proprietary process^a is its unique ability to produce solid, easy-to-handle, virgin, granular asphaltenes, which can be applied to a variety of new uses and allow for the further diversification of the petroleum sector. The utilization

TABLE 1. Proximate analysis of asphaltenes

Moisture, wt%	0.22
Ash, wt%	1.77
Volatile matter, wt%	63.64
Fixed carbon, wt%	34.37

TABLE 2. Elemental analysis of asphaltenes

Carbon, wt%	79.2
Hydrogen, wt%	8
Nitrogen, wt%	1.05
Sulfur, wt%	6.8
Nickel, ppm	339
Vanadium, ppm	877
Molybdenum, ppm	52.1
Iron, ppm	1,195
Aluminium, ppm	2,570
Cobalt, ppm	6.35
Magnesium, ppm	220
Sodium, ppm	323.4
Calcium, ppm	537.6
Titanium, ppm	446
Manganese, ppm	41.3
Cadmium, ppm	Below detection limit
Chromium, ppm	7.6
Copper, ppm	6.1
Phosphorous, ppm	41
Zinc, ppm	9,059
Silicon, ppm	3,660
Lead, ppm	Below detection limit

of asphaltenes in non-combustible ways will be critical for the long-term viability of the green petroleum sector and provides an immediate opportunity for achieving 10%–20% carbon emissions reduction from the status quo.

Asphaltene particle sizes commonly range from 100 μm –200 μm , although the process^a conditions can be modified to produce other sizes.¹¹ The bulk density of granular asphaltenes ranges from 100 kg/m^3 –200 kg/m^3 , while the softening point is above 170°C. The proximate and elemental analyses of asphaltenes derived from mined oil sands bitumen vacuum residue using the process^a are provided in **TABLE 1** and **TABLE 2**.¹²

Asphaltenes: Value-added material. Non-combustion uses have been explored for petroleum asphaltenes and asphaltene-derived products, such as carbon fibers, mats and fillers. The utility of these products for environmentally beneficial purposes, such as agricultural soil remediation and wastewater treatment, was previously discussed.¹³

In 2020, the authors' three organizations jointly examined the application of petroleum asphaltenes as a cement additive and found it to be viable as a waterproofing agent.^b Concrete is widely used in the construction of buildings and structures and comprises cement and aggregates. By design, concrete is a porous, water-wet material that allows water to pass through its matrix by hydrostatic pressure, water vapor gradients or capillary action. Over time, water can damage the integrity of concrete by several mechanisms:

1. Concretes may be susceptible to attacks from dry chemical agents when wetted
2. Internal cracks may form during freeze-thaw cycles of permeated water
3. Water infiltration may corrode or weaken the internal reinforcing materials.

To preserve the long-term integrity of concrete, waterproofing is essential and is typically applied on the positive hydrostatic pressure side of a structure. Various waterproofing techniques exist, such as torch-on membrane waterproofing (application of a polymer or asphalt), liquid membrane waterproofing (primer), sheet membranes (bonded adhesives) or epoxy application.

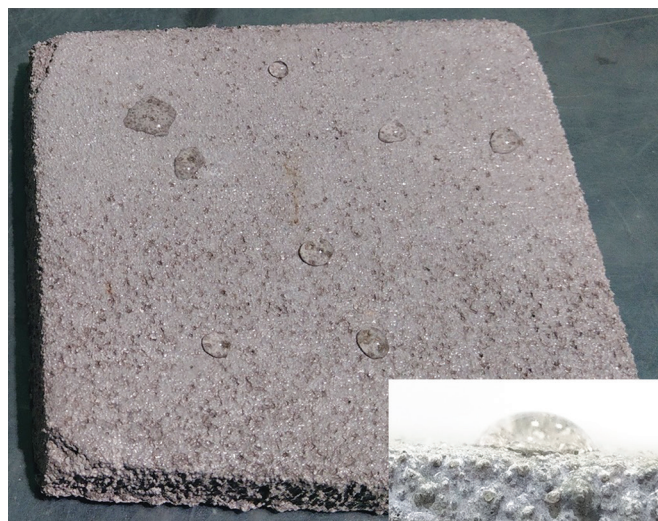


FIG. 2. Water droplets on the surface of asphalted mortar.

The development team successfully demonstrated a hydrophobic cement-matrix composite through the incorporation of 0.2 wt% asphaltenes into Taiwan cement Type 1 with standard sand and water (“asphalted mortar”). The advantage of the hydrophobic cement-matrix composite is that the cement, and by extension the concrete, becomes inherently water-resistant. Furthermore, inherently water-resistant cement-matrix composite is mold-preventative. In addition to causing structural damage, molds may cause serious chronic human health issues and negatively impact the aesthetics of buildings.

For illustrative purposes, water was applied to the surface of cured asphalted mortar. **FIG. 2** shows water droplets that remained on the surface of the asphalted mortar and a close-up view of a droplet, indicating the hydrophobic characteristics of asphalted mortar. In contrast, when water was applied to a cured mortar control group that utilized unmodified Taiwan cement Type 1, the water was immediately absorbed and percolated through the mortar sample.

The newly formulated asphalted mortar was subsequently subjected to the CNS 3763-2009 test method for waterproof agent of cement for concrete construction (**TABLE 3**). The results showed that the properties of the asphalted mortar were in compliance with CNS 3763-2009 requirements, indicating that asphaltenes are appropriate cement waterproofing agents.

Existing waterproofing techniques by which coating materials are adhered to the surface of concrete are susceptible to wear and tear and weathering, and require periodic maintenance.

The utilization of asphaltenes as cement additives presents a practical, long-term solution to enhance, supplement or even replace existing waterproofing techniques, while capturing carbon produced from petroleum streams.

Despite the long and established history of the petroleum industry, scientific and technological advancements continue to unlock valuable opportunities for stakeholders. In an actively decarbonizing society, the role of new technology will be increasingly significant as the industry seeks to balance profitability with social and environmental objectives. **HP**

TABLE 3. CNS 3763-2009 standards for waterproof agent of cement for concrete construction

Coagulating times	Initial coagulation: > 1 hr
	Final coagulation: < 10 hr
Setting characteristics	No shrinkage, expansion, cracking or warping
Strength ratio*	≥ 0.85
Water absorption ratio*	≤ 0.5
Water permeability ratio*	≤ 0.5

* Comparing properties of mortar with and without the waterproofing agent:

Control group (fluidity 111%): Cement (Taiwan cement Type 1)/standard sand/water = 1/3/0.51

Test group (fluidity 106%): Cement (Taiwan cement Type 1)/standard sand/water/asphaltene = 1/3/0.51/0.08

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NOTES

^a SELEX-Asp

^b Well Resources is the licensor of the SELEX-Asp technology. Asphaltene waterproofing additives are distributed by Shin Chuang Technology and are available under the product name "Black King Kong."

LITERATURE CITED

- ¹ Reuters, "Biden says U.S., Canada to work toward achieving net zero emissions by 2050," February 23, 2021, online: <https://www.reuters.com/article/us-usa-canada-meeting-climate-ca-idCAKBN2AO0JQ>
- ² Schaps, K., "Shell sells Canadian oil sands, ties bonuses to emissions cuts," March 9, 2017, online: <https://www.reuters.com/article/us-shell-divestiture-cdn-natural-rsc-idUSKBN16G0PH>
- ³ Williams, N., "Statoil to sell Canada oil sands assets to Athabasca Oil Corp.," December 14, 2016, online: <https://www.reuters.com/article/statoil-oilsands-athabasca-oil-idUSL1N1E92CA>
- ⁴ Williams, N. and E. Lou, "ConocoPhillips sells oil and gas assets to Cenovus for \$13.3 billion," March 29, 2017, online: <https://www.reuters.com/article/us-cenovus-energy-conocophillips-asset-p-idUSKBN1702ZR>
- ⁵ Marathon Oil, "Marathon Oil announces \$2.5 billion Canadian oil sands divestiture and \$1.1 billion Permian Basin acquisition," Press release, March 19, 2017, online: <https://ir.marathonoil.com/2017-03-09-Marathon-Oil-Announces-2-5-Billion-Canadian-Oil-Sands-Divestiture-and-1-1-Billion-Permian-Basin-Acquisition>
- ⁶ Ambrose, J., "World's biggest sovereign wealth fund to ditch fossil fuels," June 12, 2019, online: <https://www.theguardian.com/business/2019/jun/12/worlds-biggest-sovereign-wealth-fund-to-ditch-fossil-fuels>
- ⁷ Chung, K. H., Z. Xu, X. Sun, S. Zhao and C. Xu, "Selective asphaltene removal from heavy oil," *PTQ*, Q4 2006.
- ⁸ Yuan, B., Z. Tang, K. H. Chung, Q. Wei, X. Sun, S. Zhao and C. Xu, "Asphaltenes extraction treatment yields advantaged hydroprocessing feedstock," *Oil & Gas Journal*, June 6, 2016.
- ⁹ Zhao, S., C. Xu, X. Sun, Z. Xu, K. H. Chung and Y. Xiang, "China refinery tests asphaltenes extraction process," *Oil & Gas Journal*, Vol. 108, Iss. 12, April 5, 2010.

Complete literature cited available online at www.HydrocarbonProcessing.com.

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Refining Technology

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Enterprise-wide energy efficiency fleet monitoring tool

In response to challenges related to global warming, climate change and greenhouse gas emissions, numerous countries are adopting regulatory measures requiring industry to further improve energy efficiency. The authors' company has a long tradition of effectively improving energy efficiency and mitigating emissions, both for internal operational efficiency and to support external drivers within the industry—such as the API Compendium challenge—as well as managing the risk of climate change through emissions reduction goals for 2025, which are projected to be consistent with the goals of the Paris Agreement. The company continues to invest in lower-emissions technologies, such as carbon capture and advanced bio-fuels, which are necessary for society to achieve its ambition for net zero emissions by 2050.^{1,2}

Over several decades, substantial work has been done from an energy management perspective. This has enabled the company to become one of the most energy efficient international refining companies in the world and one of the most energy efficient refining companies operating in the U.S. The company has achieved a 10% improvement in energy efficiency across its global refining and chemicals operations following an effort launched in 2000³, showcasing a robust set of processes to improve energy efficiency and mitigate emissions, including programs focused on reducing methane emissions, flaring and venting. These processes include, where appropriate, setting tailored objectives at the business, site and equipment level, and then stewarding progress toward meeting those objectives. This rigorous approach is effective to promote efficiencies and reduce greenhouse gas emissions in operations, while striving to achieve industry-leading performance.⁴

However, with regulations to manage climate change risk emerging around the world, it is becoming increasingly important to develop smart ways to identify further energy efficiency

improvement opportunities in existing facilities. Such initiatives support the company's aim for industry-leading greenhouse gas performance across its businesses by 2030.¹

Energy fleets, such as fired heaters and boilers, are the primary energy consumers for refineries and petrochemical facilities. Overall facility energy efficiency improves with the improved energy performance of energy fleets. Therefore, it is important to routinely track the performance of energy-consuming equipment. This helps to identify maintenance requirements in a timely manner and improve energy efficiency.

Need for enterprise-wide monitoring tools. For an organization like the authors' company, plant performance monitoring activities consume significant resources. For example, the global fleet of fired heaters within the authors' company exceeds 700. Adding other equipment that impact the energy footprint to the fleet will result in thousands of pieces of equipment that must be monitored. It is important to deploy smart and efficient digital solutions to minimize resource requirements without affecting the quality of the monitoring. In fact, digital monitoring has helped the company to increase its overall productivity by replacing closed site level monitoring systems with open, interoperable systems. This has resulted in easier information sharing among relevant stakeholders. Such a transformation makes engineers more creative in managing fleets and unlocks many unidentified opportunities. With improved transparency, such transformation facilitates the process to monetize and prioritize opportunities at the corporate level.

Another major advantage of such an approach is that it helps to deploy a consistent process as uniform engineering toolsets are used across the entire fleet family. This also results in creating an internal benchmarking database that can be used to monetize and prioritize opportunities on a global scale.



FIG. 1. Elements of a fleet development framework.

Additionally, since an entire fleet can be on one platform, individual fleet performance can be easily rolled to corporate level key performance indicators (KPIs) that can be tracked over the period. Having such KPIs helps the corporation to develop a strategy around its energy performance.

Fleet performance presented on one visualization platform also acts as a “social proof” and psychologically motivates people to match the best demonstrated behavior. The concept of social proof is widely discussed in psychology. Cialdini⁵ coined the term to represent a phenomenon wherein people copy the actions of others to undertake behavior in a given situation. A classic example of decreasing household energy use would be to not only provide the individual’s electric consumption but also the electricity consumed by the neighbors.

Providing a common platform for sharing data will promote a healthy competitive environment and motivate all to make energy efficiency improvements.

TOOL DEVELOPMENT

The entire fleet development work process can be broken down into eight major steps, as shown in FIG. 1. The entire work process begins with the identification of the critical energy fleet population, followed by the development of a technical functional specification that acts as a backbone for the entire tool development process. This considers defining key energy performance indicators, establishing calculation methodologies, target setting and energy gap calculations.

Once tool mechanics are developed, it is important to arrange the millions of data points generated by the tool into visu-

als for easier interpretation. The last and most critical step in achieving success is to gain the trust of business partners and embed the tool into normal work processes. This sets up the tool for long-term success.

Identification. Configuring thousands of pieces of equipment into the fleet tool is resource intensive. So, for every fleet family, it is important to identify the critical fleet population based on the Pareto Principal.⁶ It is often a good idea to assign a priority for every piece of equipment to maintain a right balance between the upfront resource required and the benefits obtained by monitoring. This approach (FIG. 2) enables an organization to focus on the critical equipment first, followed by low-priority equipment when more resources are available.

One simplified approach to define priority is to sort the fleet in the descending order of energy consumption. A threshold energy consumption allows the identification of high-priority items that must be configured during an initial rollout. Minor modifications to the list are often needed depending upon equipment criticality from the process unit perspective. For example, smaller furnaces like the naphtha hydrotreater feed furnace may not be qualified based on the threshold value; however, depending on its criticality in a process unit or a site, an owner-operator may want to include it in the initial rollout.

Define KPI. This step includes the development of the technical approach defining KPIs, universally consistent estimation methodologies and target setting.

KPIs can vary depending on the family of fleet. For example, energy efficiency can serve as a KPI for equipment like furnaces, boilers and gas turbines. Different KPIs, such as thermodynamic efficiency for compressors or potential power that can be generated through steam letdown, etc., can be developed.

Once KPIs are determined, it is important to establish globally consistent methodologies to estimate the same, and to find a balance between accuracy vs. complexity of the techniques to quantify the KPI. Methods that are too complex and more accurate are usually resource intensive, as they require numerous process inputs and make the tool more complicated. Often, a literature survey or in-house research can provide such consistent techniques. For example, furnace efficiency for gas-fired furnaces can be estimated based on stack conditions, such as oxygen concentration and temperature⁷ (Eqs. 1 and 2):

$$\eta = 99 - (0.001123 + 0.0216 EA) / (T_{stack} - T_a) \quad (1)$$

$$EA = (0.98 \times 21) / (21 - O_{2stack}) \quad (2)$$

where

T_{stack} and T_a = Flue gas temperature measured at stack and ambient temperature in °F

O_{2stack} = Excess oxygen measured at stack in dry mol%

Target setting. The historical performance of the fleet in terms of KPI is valuable information in defining targets. Normally, KPI variability follows the normal variation with the fleet being operated at its best performance at least 10% of the time. A typical variability is shown on the upper left hand of FIG. 3. Minimizing the variation is the first step in improving performance, followed by pushing the mean value closer to a

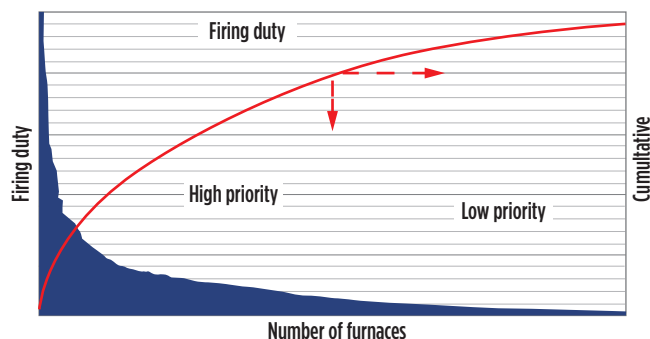


FIG. 2. Determining initial fleet population.

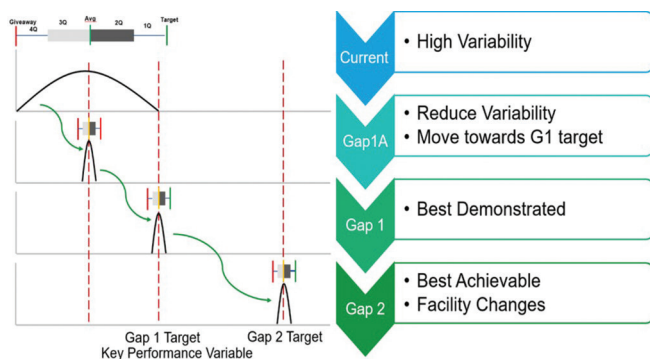


FIG. 3. Typical variability of performance parameters and how improvement is made.

constraint. The energy penalty caused due to a large variability is defined as an operational gap (GAP 1A) that can be closed through operational excellence; whereas GAP 1 is the energy penalty due to the difference between the current and the best demonstrated performance. This can be closed via engineering and maintenance excellence. Finally, GAP 2 represents the gap between the best demonstrated and the best-available technology. This gap closure often involves capital investment.

Complex fleets like gas turbines and furnaces often require understanding the impact of external parameters, such as turn-down operation on various targets, and must be incorporated in the algorithms to identify realistic gaps. For example, stack oxygen increases with furnace turndown operations due to its inherent characteristics and operability issues, raising serious safety concerns. Therefore, it is important to model oxygen targets as a function of furnace duty, as shown in FIG. 4.

Opportunity definition. It is important to show the gap between target and actual performance in terms of financial opportunity. The opportunity value helps to drive performance excellence. Engineering gaps—such as the potential energy savings and carbon dioxide (CO₂) savings if the fleet can be operated at its target—can be easily converted to an economical opportunity using the site fuel, power and CO₂ prices.

Data collection. This is the most challenging aspect of the entire process. A robust tool requires information, including instrumentation tags, equipment design information and piping and instrumentation diagrams (P&IDs). Developing a pictorial list of required instrumentations, as shown in FIG. 5, facilitates the data collection request. At times, the information might have limited availability, especially if the facility was built several decades ago. Such sites often lack sufficient instruments that are critical for KPI calculations. However, a corporate level initiative to build such systems motivates local business partners to install the desired instrumentation using cost-effective methods (e.g., wireless instruments). In a few cases, it is often required to independently infer the missing information.

Data analysis and visualization. As a part of tool development, it is important to sanitize the process information using data analytics tools. Data sanitization includes, but is not limited to, screening poor measurements, identifying the equipment running status, etc. Such an approach often provides robust KPI numbers. Inferior data input will skew the corporate level performance. Several calculation engines offered by technology companies can be used to develop process models based on functional specification.

To turn data points into actionable information, it is important to arrange these millions of data points using an adequate visualization platform. A “visual story” based on plant information can be developed that will support improvement opportunities. Various types of visuals should be considered, depending on the corporation’s requirement for action. The resulting actions taken by the operators/engineers will determine the success of the tool.

Several dashboards can be tailored to meet the requirements of the broad segment of users. Monitoring engineers, subject matter experts (SMEs) and corporate level managers are the potential users of the dashboards prepared by the tool.

Such dashboards enable spotting several improvement opportunities at various levels, and the right teams can be engaged to capture those opportunities.

A dashboard displaying information for all sites, such as the one shown in FIG. 6, promotes the social proof principle, initiating dialogue between various sites for expertise and knowledge transfer. Open dialogues between sites improve the knowledge base and best practices that are essential building blocks for the improvement. FIG. 6 shows various performance dashboards for global/regional fleet KPIs, as well as site and equipment level performance, whereas FIG. 7 shows how the dashboards can be used to identify opportunities at the equipment level. Equipment for each site can be arranged in descending order of the value of the opportunity. Alternatively, the opportunities can be viewed with a focus on the dominant cause. This helps in organizing the right teams to close the identified gaps.

Validation. This step is critical for a successful rollout of the corporate-wide tool, ensuring that relevant stakeholders are aligned and support the tool. Typically, the validation exercise requires several engagements between project engineers and the right stakeholders (site engineers, site management, corporate level energy analysts, etc.).

Depending on the corporation’s governance structure, existing work processes such as a technical quality assurance proce-

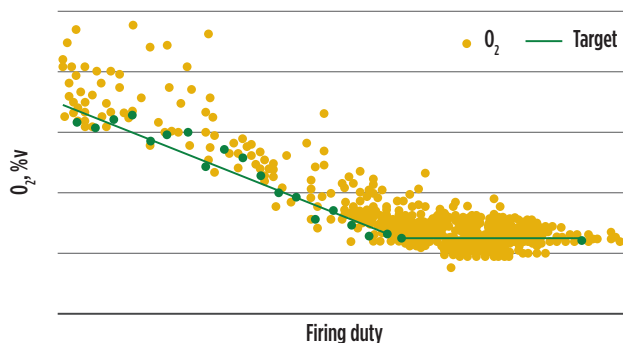


FIG. 4. Moving stack O₂ target.

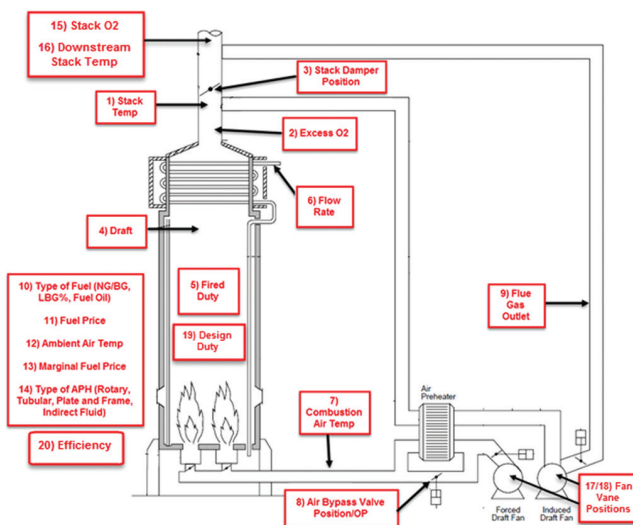


FIG. 5. Instrument tags required for monitoring a fired heater.

dures may need to be leveraged. Projects associated with closing the identified gaps should undergo an independent project review or a cold eye review. This step ensures that business partners have trust in the new system, and accept the opportunity values calculated by the tool. Trust is a key factor that can drive actions based on the tool's recommendations.

Operationalize. The focus in this final step is to embed the use of the tool on a routine basis. This will enable long-term success in extracting the most value out of the tool. This includes aligning roles and responsibilities among various departments and assigning appropriate work-process modifications to streamline the use of the tool. Integrating the tool into existing equipment monitoring work processes and energy stewardship practices will enhance the performance of the corporate-wide initiative. Depending on the corporation's governance structure, other integration opportunities must be identified to leverage them in enhancing the performance of the corporate fleet.



FIG. 6. Example dashboard.

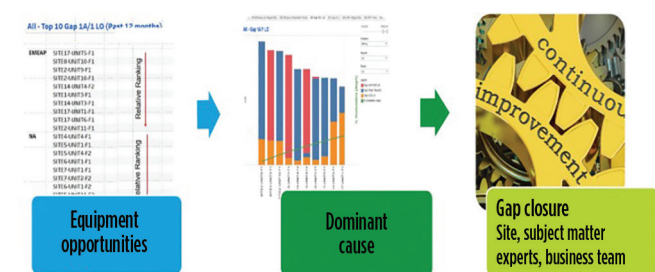


FIG. 7. Opportunity identification.

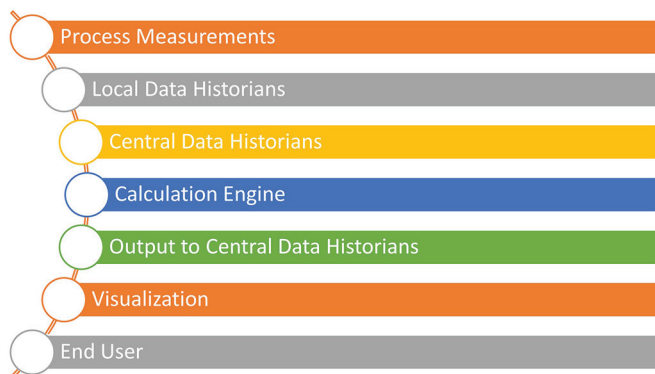


FIG. 8. Data architecture.

Data architecture. For successful digitalization, seamless data flow and connectivity are essential, especially where billions of data points are involved. This includes corporate level IT infrastructure to collect and store the information in central historians and establishing connectivity to provide secure access to the data for the entire organization. Information such as process measurements from each process unit gets historized in the data historian system. Data is accessed by the fleet tool through custom communication channels. It is important to have a powerful calculation engine that can process such information at scheduled periodic intervals, generating results and historizing to the data historian or a local database (FIG. 8). Such a database enables easy linkage with visualization software or even a web portal, creating a graphical user interface that is easy to access and use.

Applications. The authors' company widely employs the fleet monitoring tool for a variety of energy fleets, including furnaces, boilers, gas turbines, waste heat recovery steam generators, steam systems and heat exchangers. Thousands of energy consuming and producing equipment are monitored daily, benefitting the corporation. The prime advantage of such a tool for the authors' company is to drive transparency and impel action to steadily improve energy efficiency. For example, with the furnace fleet tool rollout, the authors' company has realized improved operational and maintenance discipline at sites.

The tool has identified maintenance opportunities, such as

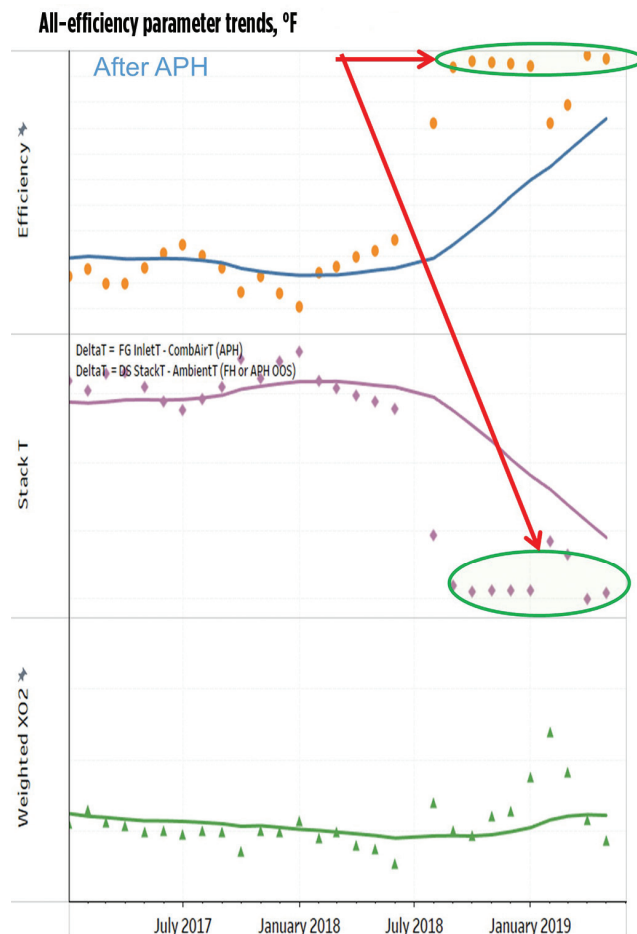


FIG. 9. Tool enables justification of air preheat replacement.

the repair of dampers and seal air leaks and the performance of regular CO breakthrough tests for turndown operations. It has also helped in identifying capital projects such as air preheater replacement. For a few items, sites are able to justify investments on an expedited basis as the associated losses are transparent to management. This has helped improve overall corporate level fleet performance.

FIG. 9 shows the air preheater upgrade project performance. The project was justified as the team was able to get historical performance from the tool and visualize the issues associated with existing technology—the technology was deemed to be outdated. By using this approach, a one-time investment in upgrading technology and equipment for the air preheater is justified that avoids the associated debit due to frequent breakdowns. **HP**

ACKNOWLEDGEMENTS

The authors would like to acknowledge the contributions of the site engineers, fired heater subject matter experts, Krishnan Chunangad, Camron Solomon, Edward Kubis, Keen Seng, Nick Smith, Phil Melancon, Bill Hicks, Nur Hidayah Md Nasir, *et al.*, for providing the help and support in developing the tool.

LITERATURE CITED

¹ ExxonMobil, "ExxonMobil sustainability report," 2020, online: <https://corporate.exxonmobil.com/-/media/Global/Files/sustainability-report/publication/Sustainability-Report.pdf>.

² ExxonMobil, "ExxonMobil announces emission reduction plans; expects to meet 2020 goals," 2020, online: https://corporate.exxonmobil.com/News/Newsroom/News-releases/2020/1214_ExxonMobil-announces-2025-emissions-reductions_expects-to-meet-2020-plan

Complete literature cited available online at www.HydrocarbonProcessing.com.



KIRTAN TRIVEDI has more than 35 yr of experience, and worked for Brown & Root Braun and Parsons before joining ExxonMobil 23 yr ago. His expertise is in process integration and energy efficiency, project planning, design and development, process simulation and reliability modeling. He has worked in technologies related to refining, ethylene, upstream gas processing, aromatics, renewable diesel, sustainable aviation fuel and methanol-to-gasoline. He earned a B.E. degree from M. S. University of Baroda, India, an M.Tech degree from the Indian Institute of Technology Bombay, India, and a PhD from the University of Adelaide, Australia, all in chemical engineering. Dr. Trivedi did his post-doctoral research at ETH Zurich, Switzerland, and is a registered Professional Engineer in California. He volunteers in organizing and chairing sessions for the AIChE Spring National Meeting and was the Chairman of Process Integration Research Consortium at the University of Manchester.



SUHAS NEHETE has 15 yr of industry experience, and worked for Reliance Industries and Shell before joining ExxonMobil 6 yr ago. His expertise is in process intensification, energy optimization and monitoring, energy and CO₂ management, and process automation. He has worked in technologies related to refining, olefins and aromatics. Mr. Nehete earned a B.E. degree in chemical engineering from the Institute of Chemical Technology, Mumbai, India. He is also registered as a Chartered Engineer by IChemE, UK.



JOHN GUNTER has worked for ExxonMobil for 31 yr, specializing in advanced process control with recent contributions to the deployment of operator guidance tools, such as abnormal event detection and procedural operations technologies. He has worked in technologies related to fuel and lubricant additives, neo acids, oxygenated fluids, polypropylene, metallocene linear low-density polyethylene films, and refining. He now works in a business planning role where new energy efficiency improvements and emissions mitigation opportunities are evaluated to support the company's goals. Mr. Gunter earned an MS degree in chemical engineering from the University of Maryland, A. James Clark School of Engineering, where he conducted pioneering research in the application of partial least squares to compositional analysis for biosensors.

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Enhanced unit monitoring enabled by digital twin

Process engineers must continuously monitor the health and performance of process units. Unit monitoring ensures reliable operation of the unit, identifies disturbances early in the cycle and improves the understanding of the process. In addition, effective unit monitoring results in the identification of short- and long-term economic opportunities. These opportunities typically reside in yield optimization, cost reduction and maximization of unit capacity.

Unit engineers use key performance indicators (KPIs) to help define and measure progress toward the plant's business and strategic goals. They facilitate the management process by focusing employees on the critical measures of the plant's performance and keeping the achieved results in open view of the staff.

KPIs are quantifiable measurements—agreed to in advance—that reflect the critical success factors of a plant. They must reflect the organization's strategic goals and must be quantifiable. The key aspect of developing KPIs is in focusing them to ensure that only those KPIs that are truly reflective of plant performance are tracked and reported.

Pacesetters use a KPI tree that tracks performance of the assets and the overall site at different levels. Each level of the KPI tree has certain objectives associated with tracking and improving the performance of the overall site. The targets in this KPI tree usually follow a top-down approach, whereas the flow of information for reporting actual performance is through a bottom-up approach.

Monitoring the performance data of process units and key equipment is one of the main inputs for the KPI tree. The rest of the information at the different levels is estimated using unit-level KPIs. In the past, unit engineers have usually relied

on raw data taken out of trends from the historian or on a laboratory information management system (LIMS). Experience in operating the unit, along with performing manual reconciliation, has been used by unit engineers to turn this into useful data; however, it is a time-consuming activity. In addition, the analysis is dependent on the individual's expertise, which is difficult to hand over to the next generation. Visibility of the analysis performed by individuals, and collaboration with peers, are also some of the challenges associated with unit monitoring.

Process digital twin. Increasing process plant complexity requires more sophisticated ways of approaching KPIs and targets. This is where real-time connected technology with deeper analytics—the process digital twin—comes to the forefront, as it accounts for the multidimensional factors and nonlinear trade-offs that make effective decision making a challenge.

These advanced analytics enable personnel to see inside assets and processes, and to perceive things that are not being

directly measured. They are wired so that insights are instantly available without data and model wrangling by end users and are run in a consistent way that everyone can understand and agree on. In this manner, the process digital twin drives agility and convergence in understanding actions across the whole business. Key inputs used for a process digital twin are shown in **FIG. 1**.

Process digital twins are created using applications that are linked to data historians, allowing them to gather and process data directly from the historian without manual intervention. The process digital twin uses a standard, automated methodology to perform the following key tasks:

- Retrieve and screen process and lab data
- Reconcile unit material balances
- Calculate key, unmeasured process variables
- Calculate a set of KPI reporting information and targets
- Assess the health of the tools, including the linear programming (LP) model

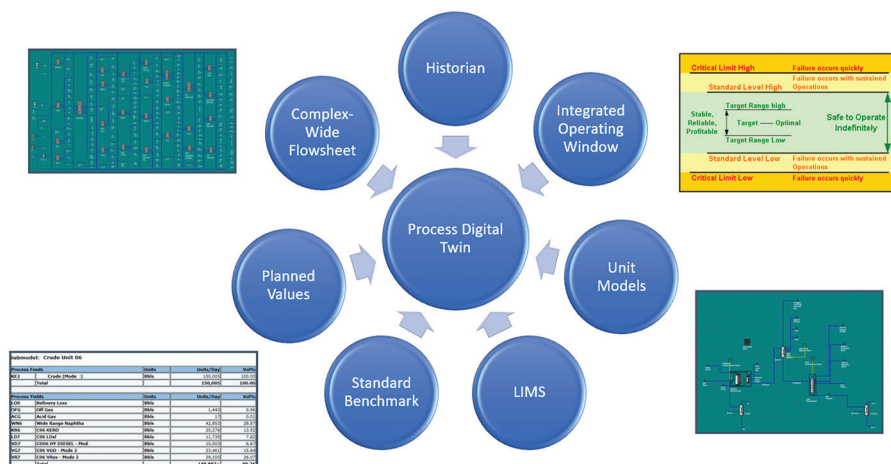


FIG. 1. Inputs used for a process digital twin.

- Generate user-configured digital reports (e.g., material balance—raw and reconciled—with data quality indicators that can trend and cross-

include complex calculations (e.g., the remaining life of catalyst). These KPIs are calculated using kinetics or equilibrium-based reactor models. Automating

indicators (MPIs), as calculated by the process digital twin, provide a comparison of the performance of tools vs. the actual unit operation. The MPIs can then be tracked in real time, improving the confidence level of the tools' users.

Unit monitoring ensures reliable operation of the unit, identifies disturbances early in the cycle and improves the understanding of the process. Effective unit monitoring results in the identification of short- and long-term economic opportunities.

plot all points and calculated KPIs over the selected time periods).

As major decisions regarding operating and optimizing the unit are performed using the data, it is essential to identify issues with the data. Relying on the raw data without checking their stability and accuracy can lead to erroneous decisions. Due to this, the leading practice is for the process digital twin to calculate data quality parameters, which automatically validates the quality of data used to estimate KPIs.

KPIs calculated by the process digital twin monitor the entire performance of the unit, and, while some of these parameters are raw or reconciled values, others

the calculations and consistent reporting saves a significant amount of time that unit engineers spend on this routine task.

One of the important uses of the process digital twin is model assurance, which ensures that the tools used for making business decisions are accurate and represent the actual performance of the unit. Process digital twins facilitate an efficient and standardized methodology for ensuring that plant data, LP predictions and nonlinear model performance are kept synchronized. Having accurate data as inputs to the LP is an important element in making good commercial decisions regarding operational changes and product planning. Model performance

first steps in reducing it. Simultaneously, variables associated with performance improvement need to be recognized.

Traditionally, refinery engineers have relied on spreadsheets and customized calculations configured by individuals. The information processed through this mechanism is accessible to selected individuals, and management lacks clarity of the information. Different versions of spreadsheets are often owned and used by isolated groups on an ad-hoc basis. Due to this critical performance, measures calculated by these groups may differ, leading to various reports with different sets of numbers being sent to management. This creates confusion throughout the organization.

To avoid confusion, utilization of the process digital twin as the analysis, calculation and reporting tool is recommended. As KPIs are calculated using first-principles models, custom-made calculations are minimized, which reduces dependencies on individuals. A centralized location is selected for the process digital twin, which is accessible to all stakeholders. The results reported can then be considered as the single version of truth. With all personnel using these results, it allows strong governance systems to avoid dependence on individuals. The flow of data through a process digital twin is shown in FIG. 2.

The most dynamic data—updated at frequent intervals—are the operating data from the process units. With continuous change in the feed quality and throughputs of the unit, the process digital twin needs to be updated at regular intervals. Other inputs can be updated on a monthly or quarterly basis, or as updated in other business systems (e.g., prices of feedstocks and products, and the integrated operating window).

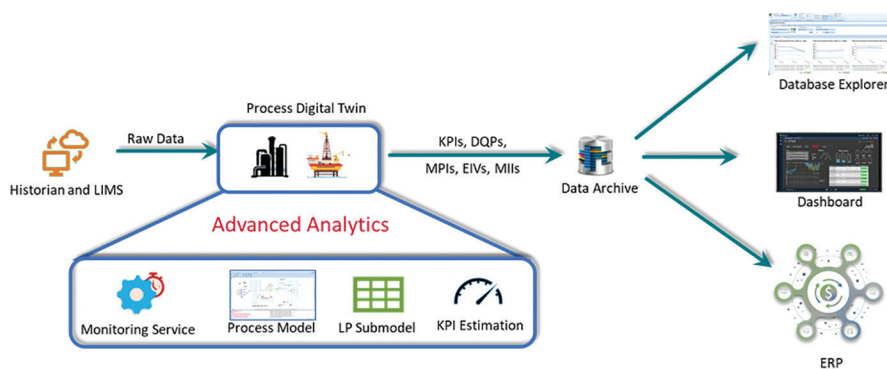


FIG. 2. Flow of data through a process digital twin.

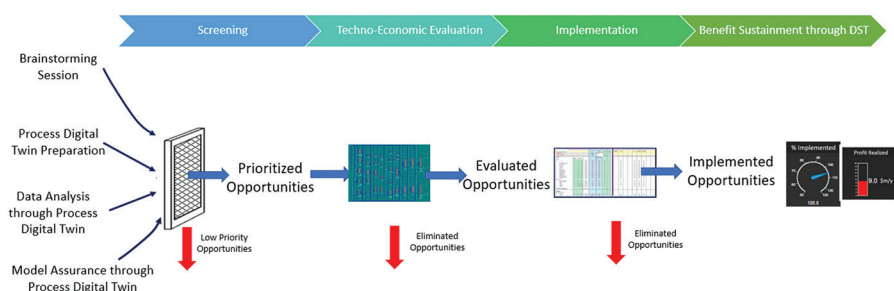


FIG. 3. Performance improvement and sustenance.

Performance improvement and sustainment. To build the process digital twin of a unit and for the overall site, it is necessary to understand the operating strategies before analyzing the data. Marginal mechanisms and constraints are identified during in-depth technical sessions and are validated using the operating data at a later stage. A brainstorming session, including the process expertise of all participants, is used to identify the gaps and opportunities.

KPIs calculated by the process digital twin often help identify additional areas for improvement. This is especially true for KPIs that are difficult to estimate and that are rarely calculated in normal operation (e.g., an approach toward equilibrium, fractionation efficiencies and flooding in distillation columns).

Process digital twins are validated on a continuous basis to provide an accurate representation of the asset over its full range of operations. Before deployment, additional insights regarding the operating trends can be found in the last few months of data. Variations of selected KPIs during a day, week or season also help identify areas that can improve performance of the process unit.

All the opportunities identified through the brainstorming session, the preparation of the process digital twin, data analysis and model assurance are screened. The opportunities are ranked based on the following criteria:

- Expected benefits from the opportunity
- Investment required
- Ease of implementation.

Qualitative analysis, rather than quantitative analysis, is performed to rank the opportunities. Based on the qualitative ranking, high-value opportunities are selected. These opportunities are pursued further for detailed techno-economic analysis, using the process digital twin as the main key evaluation tool. The opportunities are implemented, and benefits are proved through a controlled test run and demonstrated with the change in the KPIs (**FIG. 3**).

To sustain benefits from the implemented opportunities, selected margin improvement indicators (MIIs) are also configured in the process digital twin. MIIs indicate the gain or loss of margin associated with specific opportunities. The impact of MIIs is calculated using the process digital twin's ability to understand the

complex-wide benefit calculation. Monitoring of MIIs ensures that the process engineers and operators continue to optimize and benefit from the opportunity. Deviations from the targets and associated losses are reported on a continuous basis and acted upon, thereby developing a culture of profitability in the organization.

Process monitoring: Hydrocracker unit pilot. Saudi Aramco and the co-au-

thor's company collaborated to develop a pilot of Saudi Aramco's first process digital twin for the Ras Tanura refinery's (RTR's) hydrocracker unit. The pilot project was a result of a Memorandum of Understanding between Saudi Aramco and the co-author's company. The application is designed as per the unit process specifications, with the objective to monitor unit performance and continuously recommend the operational optimum. This project was a collaboration

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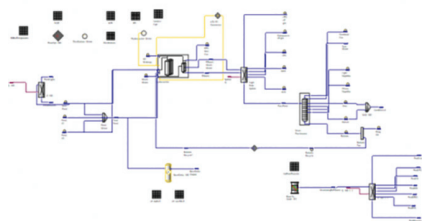


FIG. 4. Hydrocracker simulation model.

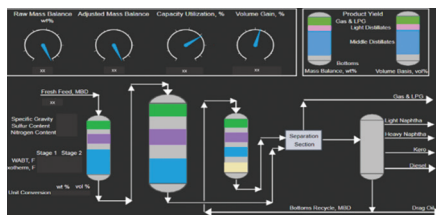


FIG. 5. Hydrocracker configuration dashboard.



FIG. 6. MIIs assign a relative dollar value to KPIs to guide unit operation.

between the RTR operations, RTR technical support, advanced solutions support and the co-author's company.

The process digital twin uses a kinetic hydrocracker reactor model to predict KPIs based on measured data. This model is also capable of predicting unmeasured KPIs, such as catalyst life and hydrogen solubility. The model also includes the effluent stripper, main fractionator, gas plant and a hydrocracker LP planning sub-model to track the RTR planning model accuracy. FIG. 4 shows the model of the hydrocracker unit.

Saudi Aramco chose not to use the co-author's company's default architecture^a because the IT policies did not support data transfer to an outside cloud. Instead, the applications were hosted on Aramco servers, with a view to transferring them to the Aramco private cloud once the pilot was completed. A proprietary dashboard was chosen to display the process digital twin results. Multiple servers were used to enable the transfer of the data from the plant and from simulations to the dashboard and to create a process digital twin. Connectivity to plant data allows automation of the process digital twin application, including retrieving plant data, running the simulation engine, executing gap calculations and other analytics.

FIG. 5 shows an overview of the dashboard representing the hydrocracker configuration. The dashboard shows plant data validating KPIs and calculated to determine the plant data quality. It also determines when an investigation is required or when the dataset can be dropped for the period of bad data. The results of the process digital twin are displayed via a dashboard.

The pilot dashboard contains multiple displays, with each display configured to present a subset of KPIs, depending on the user. For example, the model quality parameters (such as mass balance) are displayed for the owner of the process digital twin to allow maintenance when required, while the reactor and overall unit KPIs are tracked by the process engineers. Process engineers can also access higher-level KPIs, such as MIIs. The dashboard is available via an HTML interface to authorized personnel. Other dashboards include:

- Unit performance indicators, including conversion, volume gain, yields, key product properties (e.g., density, distillation, nitrogen, sulfur and flash point) and plant data quality parameters
- Reactor performance indicators, including weighted average bed temperature, exotherm, catalyst life, treat gas ratio, CFR, stage hydrogen consumption, hydrogen solubility and leakage
- Model vs. simulation vs. LP submodel performance for yields, volume gain, hydrogen consumption, distillation 90% cut points, swing cuts and/or cut point shift
- MIIs that assign a relative dollar value to KPIs to guide the unit operation (FIG. 6).

The benefits from the process digital twin include:

- Improved unit production, yield and availability
- Enhanced unit energy performance
- Identified operational risks and hazards
- Improved productivity and operational effectiveness
- Consistent and systematic monitoring of multiple sites
- Knowledge sharing between Aramco departments.

The application can easily be expanded to include tray calculation and

other equipment monitoring, as well as gap analysis on the results. In addition, data analytics can be included to calculate new LP shift vectors and other predictive analytics. The simulation model is always available to plant engineers for case studies, and the simulation data can be loaded for any past period. The results are available to authorized personnel via the web interface.

The process digital twin automates a significant portion of the process engineers' daily collection of data and KPI calculations, allowing personnel to refer to one consistent source of information. The process digital twin will allow engineers to spend more time identifying opportunities to improve refinery operations and margins, with less time validating and sorting data.

This application provides RTR engineers with a basic process digital twin of the hydrocracking unit to track the primary KPIs, including conversion, yields, catalyst life and others. The application also tracks the LP submodel performance and will enable the RTR manufacturing and planning economic unit (MPEU) to keep the hydrocracker shift vectors continuously aligned with the operation. **HP**

NOTE

^a KBC Co-Pilot

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Improve kerosene mercaptan sweetening with fluoropolymer-cartridge liquid-liquid coalescers

Many refineries are experiencing new problems related to the formation of stable emulsions and poor separation due to the increased use of lower-cost opportunity crude oils that have a high total acid number (TAN), higher gravities and more sulfur content. Various naphthenic acids, pipeline flow enhancers and injected corrosion inhibitors will distill off in the kerosene cut from the crude distillation unit (CDU). The kerosene is often treated with caustic (sodium hydroxide or ammonia) and a fixed-bed catalyst, using a proprietary mercaptan oxidation process^a for mercaptan sweetening. Sodium naphthenates will form after caustic treatment, and may foul the porous structure of the mercaptan oxidation process catalyst bed and lead to loss of production due to unscheduled cleaning operations.

Originally, a conventional batch prewash with gravity settling was sufficient treatment of naphthenic acids from low-acid-number kerosene (less than 0.02-mg KOH/g feed) and for the removal of the spent caustic from the effluent kerosene. However, the increasingly complex origin of crude blends and their associated additives—including drilling chemicals, pipeline slip enhancers and corrosion inhibitors—can result in emulsive kerosene in these simple low-TAN applications. When the acid number exceeds 0.02-mg KOH/g feed, the two phases become more emulsified due to sodium naphthenate formation. Historically, an electrostatic coalescer prewash (ECP) has been utilized to resolve the two phases. Over the past decade, electrostatic coalescers at some sites have been found to be ineffective at completely separating the aqueous caustic at several refineries (and with particular crude oils) when processing kerosene con-

taining a high TAN, corrosion inhibitors or other contaminants that result in tight kerosene/aqueous phase emulsions.

A new approach using high-efficiency, fluoropolymer cartridge liquid-liquid coalescers has been successfully pilot tested for this separation at five global refinery sites. Results from the pilot tests are presented that demonstrate the effectiveness of the high-efficiency cartridge coalescers for breaking these tight emulsions—thus reducing the caustic levels in the kerosene and providing clear and bright kerosene effluents. As a result of these improvements, spent caustic volumes can be reduced by operating with caustic strength up to 10°Bé and more fully utilized caustic than other options.

Potential benefits of the cartridge liquid-liquid coalescer approach are presented based on fouling issues in the downstream fixed-bed reactors and on increases in media life in the post-treatment section. Fouling issues can require the kerosene mercaptans sweetening process to be bypassed for several days, while the catalyst bed structure is hot-water washed to restore catalyst activity, resulting in margin losses associated with the inability to upgrade the kerosene to finished jet fuel while the reactor bed is being cleaned. A description of the first integrated, commercial pre-filter/cartridge coalescer modular unit that is ready to start up this year is provided. Immediately deployable commercial-scale rental separation equipment options are also provided.

Mercaptan oxidation process. Crude oil feeds to refineries have been trending toward heavier gravities, with increased corrosiveness, sour (sulfur) content and a higher TAN as lower-cost “opportunity”

options. To take advantage of the favorable economics associated with these opportunity crudes, many refineries have experienced new problems in various unit operations, including the slop tank area, electrostatic desalting, tower overhead corrosion, heat exchanger fouling and excessive contaminants in the plant wastewater treatment.¹ Many of these issues are related to the formation of stable emulsions and resultant poor separation due to either the absence of separation equipment or the use of ineffective physical or physiochemical separation equipment. The kerosene cut from the CDU is also an area of particular concern, as natural contaminants in high-TAN crude oil (e.g., naphthenic acids) and intentionally injected (or added) corrosion inhibitors have boiling points in this distillate cut range (302°F–482°F). These feed contaminants are known to form stable surfactant-based emulsions in refinery applications.

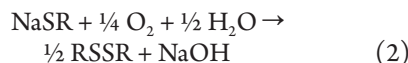
After the kerosene cut leaves the CDU, the refinery will process the stream by either steam or reboiler stripping to remove undesirable light hydrocarbons, as required to meet cut point specifications. If the kerosene has been steam stripped, then water will precipitate out of solution as the stream cools past its dewpoint. The kerosene is then treated with a dilute caustic solution (typically, sodium hydroxide), followed by a fixed-bed catalysis, using the proprietary mercaptan oxidation process. A schematic² of the mercaptan oxidation fixed-bed kerosene process is shown in **FIG. 1**.

Initially, a low-concentration caustic prewash (typically, limited to 3°Bé–5°Bé for previous technologies) is used to react with naphthenic acids that form sodium salts that have high solubility in the

aqueous phase and that are removed as spent caustic. Prewash effluent kerosene should be clear and bright with a TAN less than 0.01-mg KOH/g feed and less than 15-ppmv free water. The kerosene is then injected with air that dissolves into the hydrocarbon, providing oxygen for the mercaptan oxidation reaction in the proprietary mercaptan oxidation process reactor. The reactor contains a fixed bed that consists of a granulated activated carbon that is impregnated with a proprietary catalyst. Higher-strength caustic (typically 10°Bé) is used to provide the required alkaline environment for mercaptan oxidation. This caustic is collected in a downstream caustic settler. Any sodium naphthenates that escape in the kerosene effluent of the prewash will precipitate out of solution in the highly alkaline environment of the reactor, forming surfactants that foul the catalyst pores of the mercaptan oxidation process catalyst bed, leading to loss of catalyst activity. These surfactants also result in increased consumption of water, salt and clay, resulting in days of production losses due to unscheduled cleaning and post-treatment media replacement. In the extreme, the precipitated sodium naphthenates will increase reactor pressure drop to the point that it crushes the activated carbon base and necessitates a full catalyst replacement.

Mercaptan removal³ is achieved by reacting the mercaptan (RSH) with caustic (NaOH) to form sodium mercaptide (NaSR) and water. The NaSR product is then oxidized in the presence of the dissolved oxygen, solid-bed catalyst and caustic to produce disulfide oil (RSSR) that is then absorbed back into the hy-

drocarbon phase. The basic reactions are shown in Eqs. 1 and 2:



In the kerosene sweetening process, the disulfide oil is soluble in the kerosene, and it stays with the final product. Therefore, the sulfur content is not reduced, but the mercaptans and odor are reduced to less than maximum specifications.

ECP. The removal of the spent caustic from the kerosene is typically achieved using an ECP, with target specification of effluents being less than 1 ppmw sodium. The electrostatic coalescer operates by the basic principle that an electric field enhances the merging or coalescence of the small drops in an emulsion to form larger drops that separate faster than the smaller sizes. The mechanism for enhanced coalescence has been attributed to the creation of an induced dipole (charged droplet) by the electric field leading to dipole—dipole attraction for oppositely charged droplets in alternating current (AC) systems.⁴ For direct current (DC) systems, the mechanism for enhanced coalescence is accounted for by increased electrophoretic motion due to the electric field, whereby charged drops are attracted to oppositely charged electrodes.⁵

After the larger coalesced drops are produced, the governing settling force is Stokes' law. For the electrostatic charge to build up on the drops, the continuous fluid (hydrocarbon) should have a low conductivity and dielectric constant. If there are upsets where slugs of the aqueous

phase enter the electrical grid, the increase in conductivity and dielectric constant of the mixed-phase fluid can cause short circuits between the anode and cathode, resulting in electrode burnout, particularly if the electrodes are not insulated.

The vast majority of commercially operating electrostatic separators are designed with uninsulated electrodes, with operating conditions ranging from 12,000 V–35,000 V and 0 milliamperes (mA)–5 mA. Typically, electrostatic coalescers are designed for feedstocks containing between 0.5% and 10% inlet basic sediment and water and may have difficulty separating fine droplets in the micron size range. The advantage is that it is a proven technology with thousands of units deployed globally, and it can tolerate high levels of aqueous phase and solid contaminants. The disadvantages are that it may not be able to process feeds with high TANs, caustic strength or caustic utilization that create stable emulsions. Difficult emulsions can be broken with the use of high-efficiency liquid-liquid cartridge coalescers that have a droplet-to-fiber adsorption and agglomeration mechanism that is not present with the ECP technology. In addition, the high-efficiency liquid-liquid cartridge coalescers use a pre-filter stage that effectively removes precipitates and other solids from the kerosene stream, providing a cleaner kerosene effluent than the ECP. The ECP requires continuous phase (i.e., a hydrocarbon phase) to have a low electric permittivity. In a design with non-insulated electrodes, there is a potential risk for short-circuit and electrode damage during slug conditions.

It has become apparent at several refineries (operating with particular crudes as part of their CDU feed slates) that conventional electrostatic coalescers were ineffective at completely separating the aqueous caustic when processing kerosene containing high TAN or corrosion inhibitors that result in tight emulsions. Other refiners have interest in minimizing operating and disposal costs by operating with higher caustic utilization to minimize caustic usage and with higher caustic strengths to reduce spent caustic volume—regimes where conventional ECPs experience loss of performance. A new approach using high-efficiency, fluoropolymer-cartridge liquid-liquid coalescers has been successfully pilot tested for this application at five global refinery sites.

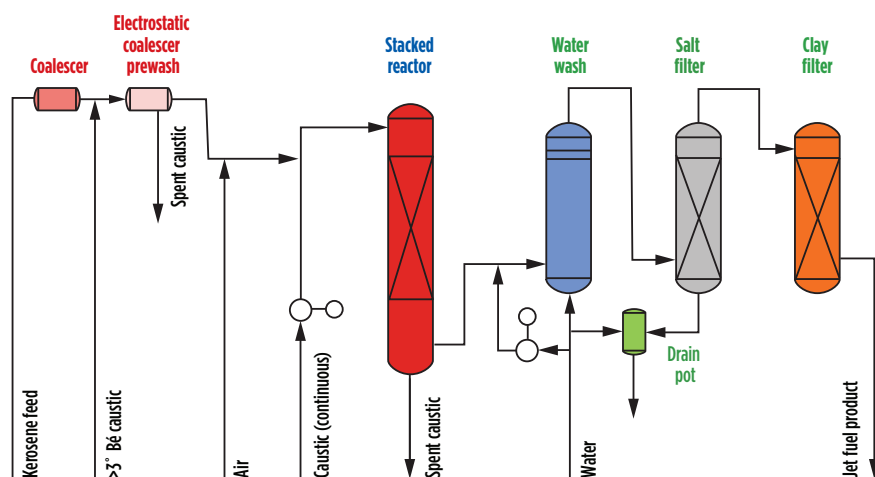


FIG. 1. Mercaptan oxidation^a fixed-bed sweetening process.

Liquid-liquid coalescer cartridge system. A high-efficiency liquid-liquid coalescer was developed for the separation of caustic from hydrocarbons using polymeric and fluoropolymer media that operate in a horizontal configuration and can separate liquids with low interfacial tensions.⁶ The overall system⁷ consists of two stages (pre-filter and coalescer) and is depicted in FIG. 2.

Pre-filter. A separate vessel with absolute-rated filter cartridges is typically used in the pre-filter stage. It is used for the separation of solids and preconditioning of the fluid. The filtration stage protects the coalescer and increases its service life. Removal of solids can also destabilize emulsions, as solids can congregate around the caustic droplets and increase the barrier to coalescing.

Coalescence and separation. The liquid-liquid cartridge coalescer system (FIG. 2) consists of a horizontal coalescer cartridge stage, followed by a settling zone that relies on the differences in density for separation of the coalesced droplets from the primary product fluid (in this case,

kerosene). The fluid enters at the left side of the housing after treatment by the pre-filter and flows from the inside of the coalescer cartridges radially outward, causing the transformation of the inlet fine dispersion of droplets into large drops in the outlet stream. This process is known as “coalescing” and can be described by the small droplets adsorbing weakly to the coalescer medium fibers, where they are subsequently subjected to collisions by incoming droplets that result in mergers and agglomerations into larger drops.

In the coalescer medium, the pore sizes are adjusted in a gradient of increasing sizes to allow for optimum growth of the drops through successive adsorptions, collisions and agglomerations. The drag force of the continuous phase flow causes the enlarged drops to disengage from the fibers. The coalesced droplets then flow in the horizontal direction (left to right) through a settling zone. For caustic removal from kerosene, the caustic phase has a higher specific gravity than kerosene; therefore, the coalesced droplets settle downward by gravity and are col-

lected in a sump located at the bottom of the housing. The purified kerosene exits the housing from a nozzle on the top-right far end of the housing.

Coalescer performance. High-efficiency cartridge liquid-liquid coalescer systems can treat streams with up to 10% inlet discontinuous phase concentrations. They can reduce the discontinuous phase down to ppm levels in the outlet and can process difficult emulsions with interfacial tensions as low as 0.5 dyne/cm. For the aqueous phase from hydrocarbon separations, coalescer outlets below 15 ppmv per a specific water testing^b method (ASTM D3240) can be achieved. The integration



FIG. 2. Horizontal liquid-liquid fiber-bed coalescer system with pre-filter.

of polymers and fluoropolymers in the coalescer materials of construction allows for expanded use of coalescers over earlier conventional types, as these advanced materials have excellent chemical resistance to an array of fluids over a wide range of temperatures from -40°F to 300°F . The advantages of these coalescer systems are that they have a small footprint, require relatively low capital investment by owner/operators and can break very stable emulsions with drops in the micron size range. They do not require electricity or chemical treatment and can be operated at

a very low turndown ratio due to a separation mechanism of direct interception. Additionally, maintenance requirements are much lower to replace coalescer or filter cartridges periodically vs. troubleshooting electrical short circuits and replacing damaged electrodes. The disadvantages are that these systems require replacement cartridges for pre-filters and coalescers, and they are not economical for mixed-phase streams with high suspended solids concentrations. Electrostatic separators vs. high-efficiency cartridge liquid-liquid coalescers are compared in **TABLE 1**.

Pilot testing high-efficiency cartridge liquid-liquid coalescers. On-site pilot testing is useful to demonstrate the performance of the high-efficiency cartridge liquid-liquid coalescers at plant conditions and to determine the optimum sizing for commercial-scale equipment. A small-scale test coalescer (typically, 6 in. in length and 2.5 in. in diameter) is used, along with a test pre-filter. The pilot test equipment is tied into the refinery process through side-stream connections and functions in a manner nearly identical to the horizontal, high-efficiency cartridge liquid-liquid coalescer system previously described. The pilot unit typically operates at a flowrate in the range of 0.5 gpm–5 gpm. Testing starts at a low flowrate that, upon verification that the effluent product is clear and bright, is subsequently increased in stages to find the point at which the coalescer performance is diminished. This point is determined visually by the haze content in the coalescer outlet samples collected in glass bottles. The amount of caustic collected vs. the total amount of kerosene is mea-

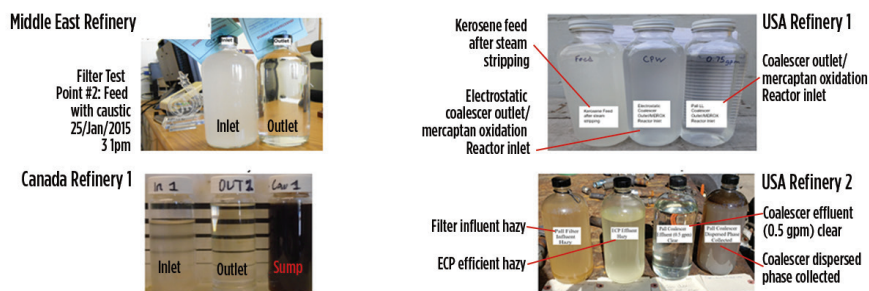


FIG. 3. Typical cartridge L/L coalescer inlet/outlet samples collected during pilot tests.

Note: The Middle Eastern refinery and the Canadian refinery are missing pictures of the ECP outlet.

TABLE 1. Electrostatic separators vs. high-efficiency cartridge liquid-liquid coalescers

Separation technology	Capital cost	Footprint	Separation efficiency	Fouling technology	Operation cost
ECP	High, typically three times that of a cartridge coalescer	Large, typically three times that of a cartridge coalescer	Limited to larger-sized droplets in coarse emulsions	Low	Low, unless subject upsets where electrode failures occur due to short circuits from slugs
High-efficiency cartridge liquid-liquid coalescer	Low	Small	Not limited, can process 1-micron droplets and larger droplets	Moderate, affected by high solids loadings	Low—typical pre-filter changeout every 3 mos and coalescer 1x per yr

TABLE 2. Results of liquid-liquid coalescer pilot tests at five refineries

Test parameter	U.S. Refinery 1	U.S. Refinery 2	Canada refinery	Middle East refinery	Asia-Pacific refinery
Inlet visible	Hazy	Hazy	Hazy	Hazy	Hazy
Outlet visible ^c	Clear	Clear	Clear	Clear (0.6 NTU)	Clear
Outlet visible ECP	Hazy	Hazy	Hazy	Hazy	Hazy
Inlet sodium, ppm	16–102	Not measured	0.07–43.6	Not measured	6–10
Outlet sodium ^c , ppm	0.01	Not measured	0.03–0.14	Not measured	0.18–0.55
Outlet sodium ECP, ppm	Not measured	Not measured	0.1–1.5	Not measured	1.38–3.3
Outlet free water ^c , ppm	12.5	10–12.5	Not measured	Not measured	Not measured
Inlet caustic phase, vol%	0.91–1.97	1.7–2.4	0.09–0.46	0.22	0.28
Maximum test flowrate, gpm	0.75	0.76	1.5	1.3	2
Caustic strength, °Bé or pH	3.5°Bé	2.4 °Bé–3.1°Bé	3.5°Bé–10°Bé	13 pH	> 14 pH
Kerosene inlet TAN, mg KOH/g	0.048	0.014	0.017–0.149	Not measured	Not measured
IFT, dyne/cm	1	8.5–12.6	4.8	Not measured	8.4
Inlet TSS, mg/l	0.4–1.2	1.1	16.5	7.6	0.5

sured, and samples are collected at the inlet and outlet of the unit for further analysis that typically includes total suspended solids (TSS), free water content, total water content, sodium content and TAN. Examples of bottle samples collected at four different refineries are provided in **FIG. 3**. These photos visually demonstrate the improved separation performance exhibited by the high-efficiency cartridge liquid-liquid coalescers over the conventional ECP separators.

Results from pilot tests at five refineries. Pilot tests were conducted at five separate refineries around the world at the caustic pre-wash section of the kerosene mercaptan oxidation process unit. The results are presented in **TABLE 2** and show several parameters measured during the field trials and in subsequent laboratory analysis. The visual analysis indicated that the inlet samples to the cartridge liquid-liquid coalescers were hazy, while the effluents were consistently clear. The outlet of the ECP units sampled all indicated a hazy appearance. The sodium levels were reduced by both the cartridge liquid-liquid coalescers and the ECP; however, where measured, the cartridge liquid-liquid coalescers reduced the sodium 3–10 times more effectively than the ECP. The free water (proprietary testing method^b) concentrations in the outlet kerosene samples from the cartridge liquid-liquid coalescers varied from 10 ppmv–12.5 ppmv.

The cartridge liquid-liquid coalescer pilot flowrates were adjusted from a low initial value up to a value where visible haze was observed, and the highest flowrate where the effluent remained clear was designated as the maximum test flowrate that is useful for scaling up the pilot results to an effective commercial system. The maximum test flowrates for the pilot cartridge liquid-liquid coalescer varied from 0.75 gpm–2 gpm under the conditions tested at the five different refineries. The caustic strength for most of the pilot tests at the caustic pre-wash locations ranged from 2.4°Bé–5°Bé, and there was one test run at a higher concentration of 10°Bé. TAN for the inlet kerosene ranged from 0.014 mg KOH/g kerosene to 0.149 mg KOH/g kerosene.

The interfacial tension (IFT) was measured and is an indication of the presence of surfactant and emulsion stability. The IFT will affect the emulsion droplet size

and difficulty of the separation and will also affect coalescer product selection and equipment sizing. The IFT was found to range from 1 dyne/cm–8.5 dyne/cm for the kerosene/caustic emulsions tested at the various refineries. TSS concentrations were measured, with a resultant range from 0.4 mg/l–16.5 mg/l.

Process benefits. The use of high-efficiency cartridge liquid-liquid coalescers will reduce the amount of caustic and naphthenate salt carryover from the caustic pre-wash step in the kerosene mercaptan oxidation^a process. Carryover of the naphthenate salts into the strong alkaline environment that is present in the mercaptan oxidation reactor bed will lead to precipitation and premature fouling of the catalyst bed. Once the mercaptan oxidation reactor is fouled, it will require a cleaning process that consists of washing with hot water over several days. If the refinery is limited by the number of reactors, then kerosene upgrading to jet fuel will

be curtailed or eliminated, and, until the mercaptan oxidation reactor is brought back online, the kerosene may be blended with refinery diesel fuel product. This can cause a reduction in profit margin at the refinery, which can be calculated by totalizing the volume of kerosene not upgraded to finished jet fuel and multiplying by the margin decrement between jet fuel and diesel. Profitability is further impacted by the additional maintenance costs of the avoidable reactor bed cleaning events.

Another potential issue that can arise in the mercaptan oxidation reactor is the buildup of the precipitated naphthenate salts, which can also lead to a high pressure drop that can crush the activated carbon, resulting in the need to replace the entire fixed catalytic bed. The associated costs for this issue include the replacement bed materials, maintenance labor and product margin losses due to downtime where jet fuel is not produced. In some cases, these emulsions can travel to the post-treatment section, causing

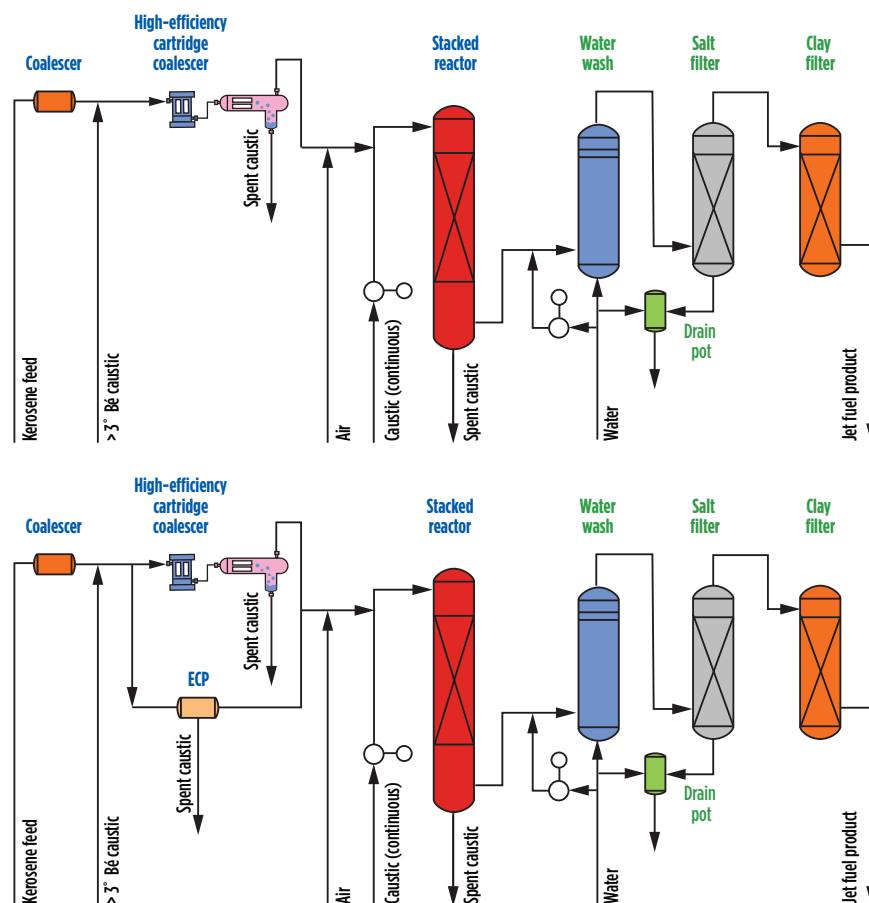


FIG. 4. Options for commercial configurations of high-efficiency cartridge liquid-liquid coalescers. The schematic shows a full replacement of an ECP (top) and in parallel with the ECP (bottom).

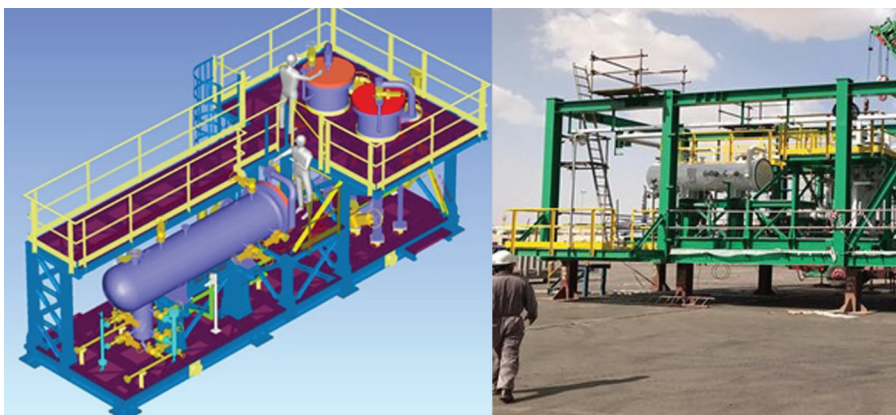


FIG. 5. CAD rendering of the first commercial unit supplied to a South American refinery (left) and the completed module being installed at the refinery (right).



FIG. 6. Proprietary high-efficiency horizontal liquid-liquid coalescer rental unit^d.



FIG. 7. Proprietary duplex, horizontal pre-filter rental unit^e.

increased water, salt and clay changeout frequencies, and thus requiring additional unplanned downtime and financial losses.

A final additional cost to consider is connected to the operation of the ECP where caustic slugs or upsets occur. These conditions can lead to the electrical grids shorting out, which will require premature maintenance for replacement. Depending on the availability of components, significant lead times may be required, and the limitations on jet fuel production may be protracted, thereby deepening product margin losses for the refinery. The associated costs include replacement parts, maintenance labor and margin losses due to bypassing or curtailing jet fuel production.

Commercial options. The use of high-efficiency cartridge liquid-liquid coalescers can be deployed in two ways. The ECP can be completely replaced, allowing the cartridge coalescer to process the full kerosene flow, or the coalescer can be used in parallel to the ECP, processing a portion of the total kerosene flow to allow the ECP to operate at a flowrate that is low enough to significantly improve its performance and the reactor protection it is intended to provide. Schematics² of these options are depicted in **FIG. 4**.

The advantage of using the full-flow option is that it will be more flexible in separating tougher emulsions that can be created by a higher TAN content in the inlet kerosene feed or by using a higher concentration of caustic that may be desirable to reduce waste disposal costs. The use of the cartridge liquid-liquid coalescer in parallel to the existing ECP may be beneficial for cost reductions, given that this arrangement would require smaller cartridge coalescer equipment.

First commercial unit. The first commercial unit for applying the high-efficiency cartridge liquid-liquid coalescers to the mercaptan oxidation kerosene caustic pre-wash has been supplied to a refinery in South America and is expected to be commissioned in mid-2022. The unit consists of dual vertical pre-filters that contain absolute-rated particle filters followed by a horizontal liquid-liquid coalescer vessel that contains fluoropolymer-type coalescer cartridges. The system will operate with one filter online and one in standby mode to allow continuous protection of the coalescer cartridges from particulate fouling. The coalescing system is designed for a flowrate of 10,000 bpd (292 gpm). A CAD-rendered

schematic of the integrated pre-filter/coalescer module alongside the actual, fabricated equipment being installed at the refinery is provided in **FIG. 5**.

Rental units. In addition to a permanent installation, another option is the implementation of rental pre-filter and cartridge liquid-liquid coalescer skids. This allows refineries to quickly install a filter and/or liquid-liquid coalescer skid to solve a fouling or quality problem. The time frame for rental unit deployment is days to weeks vs. months to years for purchased, custom-engineered, permanent equipment. A fleet of rental skids is available that generally meets or exceeds refinery specifications. These skids are large enough to handle most process flows, while providing acceptable filter life and liquid-liquid coalescer performance. Examples of a proprietary liquid-liquid coalescer rental skid^d and a proprietary pre-filter rental skid^e are provided in **FIGS. 6** and **7**, respectively.

Takeaway. The use of high-efficiency cartridge liquid-liquid coalescers was clearly demonstrated as an improved alternative to ECP through successful onsite pilot trials at five global refineries where high-TAN (greater than 0.025 mg KOH/g feed) kerosene was present. This cartridge coalescer technology, which provides enhanced separation of the caustic and naphthenic salts over the ECP, has a significantly lower associated capital investment and a much smaller footprint. The process benefits related to reduced carryover of the contaminants contained in these caustic-washed kerosene streams include a dramatic reduction in fouling issues in the mercaptan oxidation reactor bed and the ensuing reduction in unit downtime (and in lost jet fuel production margins) resulting from avoidance of excessive hot-water washing to restore reactor permeability. The onset of increased differential pressure—and the risk of crushing the activated carbon bed granules in the reactor, requiring replacement and associated costs—will also be greatly reduced.

The first commercial high-efficiency cartridge liquid-liquid coalescer unit has been delivered to a South American refinery and is slated to start up operations by 2022. The two different approaches for installation of the cartridge liquid-liquid coalescers are to fully replace the

ECP and to treat the full kerosene flow or to run in parallel with the ECP (using a smaller cartridge coalescer for a portion of the total kerosene flow). A skid rental may also be considered as an alternative to custom-engineered, permanent equipment for either approach. **HP**

NOTES

^a Honeywell UOP's Merox process

^b Gammon Corp's AquaGlo

^c Pall Corp.

^d Pall Corp.'s horizontal liquid-liquid coalescer rental unit

^e Pall Corp.'s duplex, horizontal pre-filter rental unit

LITERATURE CITED

¹ Qing, W., "Processing high TAN crude: Part 1," *PTQ*, Q4, 2010.

² Honeywell UOP, "Fixed-bed caustic Merox process unit training class," 2020.

³ Basu, B., S. Satapathy and A. K. Bhatnagar, "Merox and related metal phthalocyanine catalyzed oxidation processes," *Catalysis Reviews: Science and Engineering*, 1993.

⁴ Taylor, S. E., "Theory and practice of electrically enhanced phase separation of water—Oil emulsions," *Transactions of the Institute of Chemical Engineers*, 1996.

⁵ Midtgard, O. M., "Electrostatic field theory and circuit analysis in the design of coalescers with pulsed

DC voltage," *Chemical Engineering Journal*, 2009.

⁶ Wines, T. H. and R. L. Brown, "Difficult liquid-liquid separations: High-performance, polymer-fiber coalescers break up hard-to-handle emulsions and dispersions," *Chemical Engineering*, December 1997.

⁷ Wines, T. H., and S. Mokhatab, "High-efficiency coalescers for gas processing operations," *PTQ*, Q4 2017.

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Deliver high levels of SO_x reduction with SO_x-reduction additive

The global refining industry continues to move toward more restrictive environmental laws for sulfur oxide (SO_x) emissions. In addition, many refineries are looking to maximize fluid catalytic cracking unit (FCCU) profitability by processing more challenging feedstocks that are higher in sulfur, or using SO_x reduction additives to reduce caustic consumption in the wet gas scrubber for overall OPEX reduction. As such, SO_x emissions control remains a crucial topic for refineries to ensure competitiveness in the market. The authors' company recognizes this and has recently allocated considerable resources to developing the latest generation of SO_x reduction additives.

A new FCC additive technology^a for SO_x reduction has been successfully commercialized. The SO_x reduction additive incorporates a more homogeneous distribution of cerium and vanadium across the additive particle, as well as an increase in the magnesium aluminate spinel content of the additive. Since its introduction, several refiners have switched from general SO_x reduction additives to the proprietary SO_x reduction additive^a due to the step-out improvements in performance.

The BP Rotterdam refinery recently began using the proprietary additive. This refinery initially switched from a general SO_x additive to another of the authors' company's additives^b, followed by the aforementioned SO_x reduction additive^a. Both additive changes resulted in an increase in SO_x reduction.

SO_x additive development. In 2018, the authors' company made a modification at its SO_x additive manufacturing facilities, which required significant capital investment. The result is an improved

version of its additive^b for SO_x reduction, with improvements to both product properties and performance. The new SO_x additive was initially referred to by another name^c to signify the improvement in cerium and vanadium dispersion across the additive particle. However, based on commercial performance, the new additive technology is being branded^a to better reflect its step-out performance.

Cerium and vanadium dispersion play an important role in SO_x additive performance. Improved dispersion of these key active ingredients results in a more effective oxidation of sulfur dioxide (SO₂) to sulfur trioxide (SO₃), and enhances the additive regeneration step where the sulfate is reduced to hydrogen sulfide (H₂S), both of which are key steps in the SO_x reduction mechanism.

For the development of SO_x reduction additives, the authors' company utilizes larger scale test equipment, specifically the Davison circulating riser (DCR) pilot plant.¹ Such a pilot unit provides valuable information based on a continuous operation. Additionally, compared to bench-scale units, the DCR pilot plant has the advantage in that it mimics all the processes present in a commercial operation and can also operate at the same hydrocarbon partial pressure as a commercial unit. The continuous catalyst regeneration in the DCR allows for the measurement of regenerator SO_x and nitrogen oxide (NO_x) emissions and testing of environmental additives, experiments that cannot be done in a batch unit.

FIG. 1 shows DCR pilot plant testing comparing SO_x reduction performance for SO_x additives with less-dispersed vanadium and cerium vs. the same SO_x additives with a higher level of dispersion. The pilot plant testing was initially oper-

ated without an SO_x additive to establish the baseline level of SO_x, then at "Time = 0 hr" the SO_x additive was introduced in a single dose to observe the initial level of SO_x reduction. The subsequent period of time required for the SO_x emissions to increase back to the baseline level of SO_x was used as a measurement for the additive's effectiveness for SO_x reduction.

The additives with high and low vanadium dispersion were tested at the standard level of 1 vol% oxygen (O₂), and the results highlighted that both additives showed the same initial level of SO_x reduction, but the additive with a higher level of vanadium dispersion retained the SO_x reduction activity for a longer period of time.

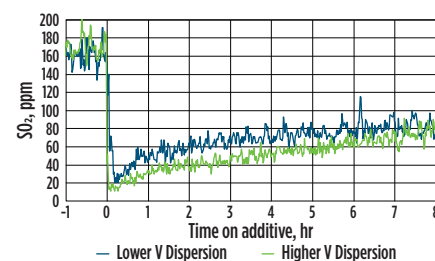


FIG. 1. Impact of vanadium dispersion on SO_x additive performance.

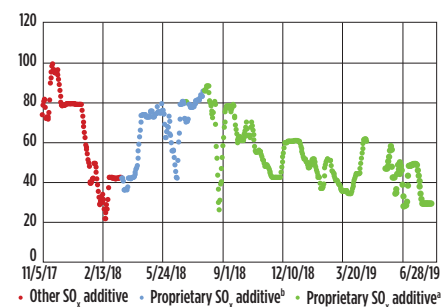


FIG. 2. The 7-d average SO_x additive rate (normalized).

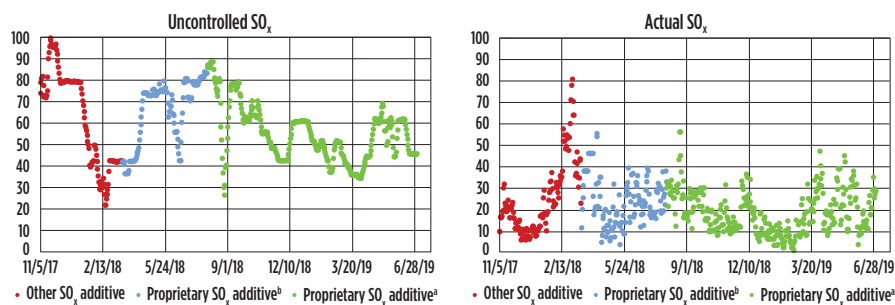
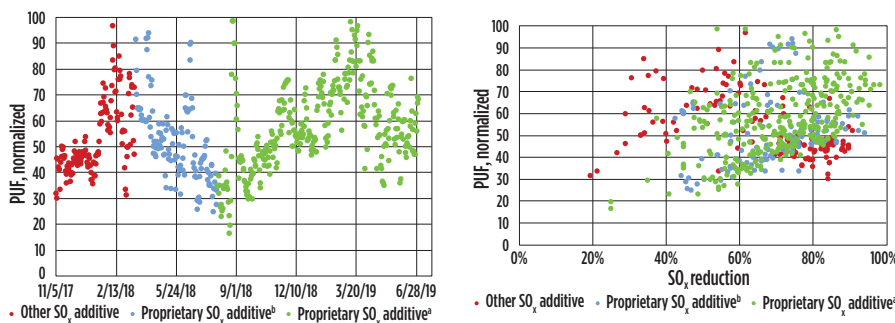


FIG. 3. SO_x emissions level (normalized to highest uncontrolled SO_x).



FIGS. 4 AND 5. PUF plotted against time and % SO_x reduction.

SO_x additive performance at BP Rotterdam. The BP Rotterdam refinery uses an SO_x additive on an ongoing basis to comply with SO_x emissions limits. In March 2018, the refinery elected to change from a general SO_x additive to the proprietary SO_x additive^b, later changing to the newly developed additive^a. The following case study describes how these SO_x additive changes impacted SO_x emissions control.

The BP Rotterdam FCCU is a challenging operation in terms of SO_x additive performance. Specifically, the low oxygen level in the regenerator is likely to be a limiting factor for SO_x additive performance due to the oxidation of SO_2 to SO_3 being a bottleneck in the SO_x reduction mechanism. This is reflected in the relatively low pick-up factor (PUF) values observed. It is also worth noting that the Rotterdam FCCU's highly variable feed properties can make the evaluation of SO_x additive performance more challenging. For this reason, a multi-variable regression analysis was performed. This statistical analysis seeks to establish the relationship between dependent and independent variables. Developing a robust multivariable regression allows the evaluation of additive performance despite many changes occurring simultaneously.

FIG. 2 shows the daily SO_x additive usage rate from November 2017 through the SO_x additive^a trial. Using a seven-day (7-d) rolling average is a useful way to look at the SO_x additive rate, as it helps to smooth out large differences in the daily addition rate, enabling a more meaningful comparison of PUFs. The average usage rate of the SO_x additive^b was slightly higher than the previous additive due to pre-blending with fresh FCC catalyst, which coincided with a period of higher catalyst addition rate. The average addition rate for the latest SO_x additive^a was 15% lower than the general additive period.

The uncontrolled levels of SO_x (i.e., the SO_x level that would be obtained without using an additive) are calculated using a correlation based on the wt% sulfur in the net slurry product. FIG. 3 shows the uncontrolled SO_x levels vs. actual SO_x levels observed during the different periods (the values are normalized to the highest uncontrolled SO_x level). The actual SO_x levels were maintained at low levels during the use of the proprietary SO_x additives^{a,b}. The overall SO_x reduction increased from 67% to 70% with the use of one SO_x additive^b, then increased further to 73% using the newest SO_x additive^a.

As a performance indicator when as-

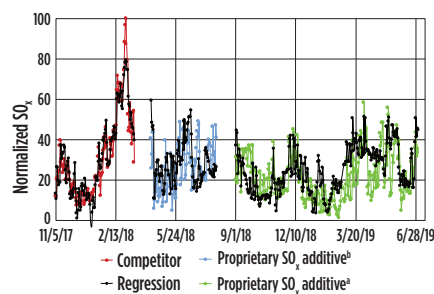


FIG. 6. Comparison of actual SO_x levels vs. calculated SO_x from regression analysis.

sessing SO_x additive performance, the PUF is a calculation of mass of SO_x captured per mass of SO_x additive used, and is a measure of SO_x additive effectiveness. A PUF value for a given application can fluctuate depending on various factors. For example, the PUF would be expected to decrease when achieving a higher percentage of SO_x reduction as the concentration of available SO_x molecules becomes lower.

Therefore, with the higher percentage SO_x reduction achieved with the proprietary SO_x additives^{a,b}, a lower PUF might have been expected. However, FIGS. 4 and 5 show that the expected drop in PUF was not observed. In fact, for a given percentage of SO_x reduction, the additives even resulted in a slightly higher PUF, which is testament to the SO_x reduction performance being achieved.

As previously mentioned, multi-variable regression analysis can be useful for evaluating SO_x additive performance, as it considers changes that are occurring in the operation.

Such an analysis was performed to establish a correlation for calculating the expected SO_x emissions during the period of using a general additive. The analysis identified three key variables or predictors for SO_x emissions (ppm): slurry sulfur (wt%), SO_x additive rate (kg/d) and excess oxygen (vol%). The formula established below results in a high R^2 value of 90%, indicating that this regression analysis can accurately explain the variation of SO_x emissions using the specified predictors. The definition of R^2 being the percentage of the response variable variation (calculated SO_x) is explained by the three key variables.

These three key variables are well-known in terms of impact on SO_x emissions. Slurry sulfur levels typically correlate well with coke sulfur levels, which is

the direct precursor for the uncontrolled SO_x emissions. The SO_x additive rate is an obvious parameter for SO_x emissions reduction, while the excess oxygen level typically has an effect on SO_x additive performance, particularly at the low oxygen levels at which the Rotterdam FCCU runs.

The correlation for calculating actual SO_x emissions using a SO_x additive:

- Calculated SO_x (ppm) =
 $-119.33 + 326.72 * (\text{slurry sulfur, wt\%}) - 0.41 * (\text{addition rate, 7-d average kg/d}) - 14.21 * (\text{O}_2, \text{vol\%})$

FIG. 6 shows the SO_x emissions calculated using the regression (in black). These data points overlap closely with the actual SO_x emissions during the period of using a general additive. The analysis highlights that on average compared to the general additive, the proprietary additive^b resulted in 6% lower SO_x emissions, while the newest proprietary additive^a reduced SO_x emissions by 12%.

Takeaway. Through improved cerium and vanadium dispersion, as well as increased spinel content, the authors' com-

pany's SO_x reduction additive^a is delivering improved levels of SO_x reduction performance in multiple back-to-back additive trials. More than 15 refiners globally have now successfully trialed the new additive vs. the general additive. The investment made in the commercialization of the new additive highlights the commitment to developing new FCC additive technology as part of the authors' company's continued focus on its FCC product portfolio. The case study described at BP Rotterdam demonstrates the high levels of SO_x reduction performance that is possible, based on both unit operating data and multi-variable regression analysis.

As described, the new FCC additive technology^a has been applied successfully in BP Rotterdam's full-burn FCCU. This new additive has also been successfully trialed in partial-burn FCCUs, which will be described in upcoming articles. **HP**

LITERATURE CITED

- ¹ Habib, T. and K. Bryden, "Flexible pilot plant technology for evaluation of unconventional feedstocks

and processes," AFPM Reliability & Maintenance Conference and Exhibition, Orlando, Florida, 2013.

NOTES

^a W. R. Grace & Co.'s EMISSCIAN™

^b W. R. Grace & Co.'s Super DESOX®

^c W. R. Grace & Co.'s Super DESOX® CV+



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Avoid common pitfalls in upscaling catalytic fixed-bed reactors

Driving innovation is an inescapable strategic reality, not only for accelerating new products development and technological solutions but also for creating new markets. Multidisciplinary collaborations—such as research and development, business and marketing, and engineering—are indispensable to define potential business and market share targets. The development speed of new products is very demanding because the needs of customers have been influenced by rapid disruptive changes.

In the early stages of so-called product conceptualization, the purpose of a new product or technology must match the company's direction to compete in the world market. Effective synergistic collaboration between multidisciplinary functions is a key success factor in this stage of development. Development must be based on numerous information exchanges between specialists, researchers and engineers to conceptualize the commercial process, including optimal operating conditions for large-scale production.

Challenges in dissimilarity of mass throughput. A commercial reactor is usually designed to deliver high throughputs to maximize profits while minimizing total investment cost. Conversely, laboratory and pilot reactors are commonly used for experimentally investigating new phenomena and producing the necessary information that is applicable or adaptable to the upscale design of new—or the improvement of existing—commercial processes and facilities. The utilization of laboratory and pilot units with low mass throughput is inevitable due to:

- Minimizing total investment and economic risk
- Maintaining flexibility for frequent reconfiguration
- Widening operating range
- Easing handling and waste disposal
- Decreased concern and smaller risk of safety and environmental impacts
- Increasing project speed, including smooth startup and shutdown.

It is logical that the flow regimes inside laboratory, pilot plant and commercial reactors are significantly different. Generally, the flow regime of fluid can be classified into three types: laminar, transition and turbulent flows. As expected, this flow regime dissimilarity can significantly impact the observed catalyst performance in a heterogeneous (solid-fluid) catalytic reactor. The following section will focus on the fixed-bed reactor, as it is the most commonly used.

Rate-controlling mechanisms and flow behavior. By focusing on a typical porous catalyst pellet packed in a fixed

bed, several sequential and parallel mass transfer and reaction steps can be seen, as illustrated in **FIG. 1**.¹

- Step 1: Reactants transfer from the bulk fluid stream through a stationary film to the external surface of the pellet
- Step 2: Reactants next diffuse into the pores to catalytic sites on the internal walls
- Step 3: Reactants adsorb on the active sites
- Step 4: Reactants are converted to products via surface reaction
- Step 5: Products desorb from the active sites
- Step 6: Products next diffuse inside the pores to the pellet external surface
- Step 7: Products transfer from the pellet surface through the film to the bulk fluid stream.

For most heterogeneous catalytic reactions, it is reasonable to assume that the first-order surface reaction, as well as very fast adsorption and desorption steps, control the overall reaction rate. Making use

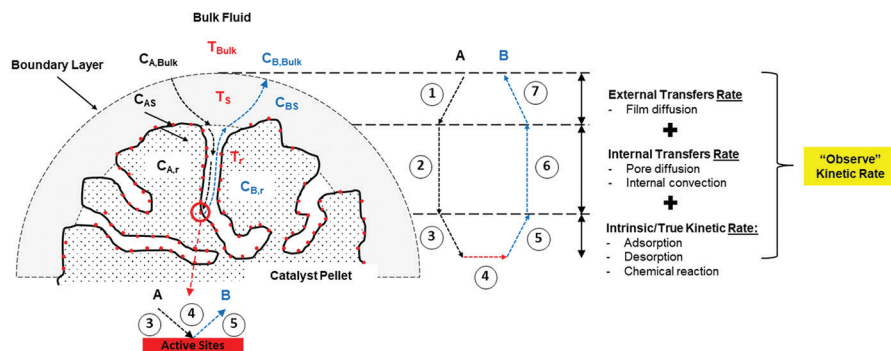


FIG. 1. General steps of heterogeneous catalytic fluid-porous solid reaction, and an illustration of concentration profile of Reactant A and Product B.

of pseudo-steady-state approximation, the following relation between the ob-

resistance of the stationary film around the pellet is dominant, and this becomes

Generally, the effect of temperature on the observed (or apparent) activation energy is investigated by carrying out experiments in a laboratory reactor at sufficiently high fluid velocity to ensure a reasonably fast film diffusion rate. Nevertheless, in the significantly high temperature range using catalyst powder, the film diffusion step would become rate-limiting and the observed global reaction resistance becomes more or less proportional to

During each stage of upscaling of a new process/product development—from catalyst development and testing at laboratory and pilot scales to the up-scaled design and adiabatic operation of a corresponding commercial reactor—an unsuspected shift of the rate-controlling step is a common prevalent pitfall to be handled appropriately.

served global, film-diffusion, pore-diffusion and true-kinetic rate coefficients can be derived (Eq. 1)^{1,2}:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{intr}}} + \frac{1}{k_{\text{PD}}(a_p/v_p)} + \frac{1}{k_{\text{FD}}(S_c/V_c)} \quad (1)$$

The effect of internal diffusion on the observed reaction rate can be considered by the so-called effectiveness factor (η), which is defined as “the ratio of the real reaction rate of the catalyst particle to the imaginary reaction rate when the whole particle is assumed to bathe in the surface reactant concentration.” Meanwhile, the effects of fluid velocity and flow regime can be represented as a function of the pellet-based Reynolds (Re) number. Eq. 1 can therefore be transformed to Eq. 2:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{\eta k_{\text{intr}}} + \frac{\psi}{Re_p^n} \quad (2)$$

As shown in **FIG. 2**, laboratory and pilot reactors, which are generally small in size and designed for low mass throughput, frequently exhibit a laminar-flow regime. As a result, the mass transfer

the rate-limiting step. The film resistance dramatically decreases when the flow regime becomes highly turbulent, as is typical in a commercial reactor. In other words, this shift from film diffusion-rate controlling to pore diffusion-rate or surface-reaction controlling generally occurs when upscaling to a high-capacity commercial reactor. Pore diffusion rate will dominate when the pellet size is relatively large or the internal catalytic sites have very high reactivity.

Rate-controlling mechanisms and temperature. Another major difference between laboratory/pilot and commercial reactors is the effect of heat loss on the surrounding area during operation. Due to a high surface area per volume of tubing and small piping, as well as a small quantity of reaction heat generation (or absorption) corresponding to low mass throughput, most laboratory and pilot reactors are run isothermally, in practice. Their superficial fluid velocity is relatively low and the flow regime is mostly laminar or (at most) transitional.

Conversely, the corresponding effect of significant heat loss in a large-column commercial reactor with huge mass throughput is essentially negligible. Therefore, these reactors are generally designed and operated in adiabatic mode. Their superficial fluid velocity is quite high and the flow regime is mostly turbulent. The implication is that the rate-limiting step for the former reactors is typically film diffusion (particularly true at high reaction temperature), whereas for the latter it is pore-diffusion and/or surface reaction. Since this discussion is focused on individual catalyst pellets, the influence between isothermal and adiabatic operations is not considered here.

the external mass transfer film resistance. From Eq. 2, we obtain Eq. 3:

$$\frac{1}{k_{\text{obs}}} \approx \frac{\psi}{Re_p^n} \quad (3)$$

Since the gas density and viscosity depend only slightly on temperature, so does the corresponding Reynolds number. In other words, according to Eq. 3, the experimentally determined apparent activation energy should be quite small. Conversely, in the low temperature range, the rate of reaction becomes very slow and therefore the rate-limiting step. The determined activation energy becomes essentially equal to the true activation energy defined by the Arrhenius law.

In the intermediate temperature range using a typical commercial catalyst pellet, the pore-diffusion step becomes rate-limiting. From Eq. 2, we obtain Eq. 4:

$$\frac{1}{k_{\text{obs}}} \approx \frac{1}{\eta k_{\text{intr}}} \quad (4)$$

The effectiveness factor in the case of an irreversible n -th order reaction is given by Eq. 5:

$$\eta \approx \frac{3}{(d_p/2)} \sqrt{\frac{D_e}{k_{\text{intr}} C_{As}^{1-n}}} \sqrt{\frac{2}{n+1}} \quad (5)$$

Substituting the effectiveness factor from Eq. 5 into Eq. 4 yields Eq. 6:

$$k_{\text{obs}} \approx \frac{3}{(d_p/2)} \sqrt{\frac{D_e}{k_{\text{intr}} C_{As}^{1-n}}} \sqrt{\frac{2}{n+1}} \times k_{\text{intr}} \quad (6)$$

Applying the Arrhenius equation to k_{obs} and k_{intr} in Eq. 6, Eq. 7 is obtained after simplification:

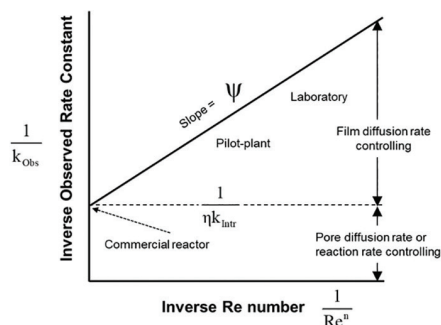


FIG. 2. The relationship between the inverse observed kinetic rate constant and inverse Re number that represents flow behavior in isothermal operation.

$$\ln[A_{\text{obs}}] - E_{A,\text{obs}} \frac{1}{RT} = \ln \left[\frac{3}{(d_p/2)} \sqrt{\frac{2D_e}{(n+1)}} C_{As}^{1-n} \times A^{1/2}_{\text{true}} \right] - \frac{E_{A,\text{true}}}{2} \frac{1}{RT} \quad (7)$$

Since the second term on the left hand side corresponds to that on the left hand side, Eq. 7 indicates that the apparent activation energy in the case of pore-diffusion control is approximately half of the true activation energy (Eq. 8):

$$E_{A,\text{obs}} \approx \frac{E_{A,\text{true}}}{2} \quad (8)$$

FIG. 3 displays the effect of temperature on the observed global rate constant, as well as the region of each rate-limiting step and its observed apparent activation energy.

The unintentional shift of the rate-controlling step over temperature variation represents another common pitfall in the design scale-up of fixed-bed reactors for highly exothermic and endothermic reactions. Due to the unavoidable difference in flow regimes between laboratory/pilot reactors operated isothermally and commercial reactors operated adiabatically, experimental data obtained in the lab reactor are useful for determining the true reaction kinetics and reaction scheme; those obtained in a small-scale pilot reactor are useful for investigating the conditions closer to the commercial unit.

However, both types of data are often insufficient for upscaling to a commercial adiabatic reactor. In practice, the commercial reactor is frequently designed at a highly turbulent flow through a packed bed of catalyst pellets to attain high throughput with acceptable pressure drop. Therefore, pore diffusion generally becomes the rate-limiting step. When adiabatic operation is adopted, an unintentional shift from pore diffusion control to film diffusion—or, more frequently, intrinsic rate control—is likely to occur, especially when a large temperature difference exists between the inlet and outlet of a catalyst bed. As a result, the designed reactant conversion and/or product selectivity may not be achieved if the facilities and reactor are designed without considering the above-mentioned shift.

Another common pitfall is the substantial reduction of catalyst size in case of exothermic reaction to increase production rate by minimizing pore diffusion limitation. This may lead to a runaway reaction and can be handled by reducing the catalyst pellet to an optimal size. However, if the reaction is highly exothermic, the adiabatic reactor may have to be replaced by a multi-tubular reactor with internal cooling.

A handy scaling correlation applicable for non-isothermal reactors.

To enhance the upscaling success rate, the effect of the three common rate-controlling steps on the observed global rate as a function of flow behavior and temperature must be clarified. From Eq. 5, if the reaction order can be approximated as pseudo-first-order ($n = 1$), the effectiveness factor becomes (Eq. 9):

$$\eta \approx \frac{3}{(d_p/2)} \sqrt{\frac{D_e}{k_{\text{intr}}}} \quad (9)$$

The substitution of Eq. 9 into Eq. 2 yields (Eq. 10):

$$\frac{1}{k_{\text{obs}}} = \frac{1}{\frac{3}{(d_p/2)} \sqrt{D_e} (k_{\text{intr}})^{1/2}} + \frac{\psi}{\text{Re}_p^n} \quad (10)$$

The Arrhenius form of the intrinsic rate constant is (Eq. 11):

$$k_{\text{intr}} = A_{\text{True}} \exp \left[\frac{-E_{A,\text{true}}}{RT} \right] \quad (11)$$

Substituting Eq. 11 into Eq. 10 yields (Eq. 12):

$$\frac{1}{k_{\text{obs}}} = \frac{1}{\frac{3}{(d_p/2)} \sqrt{D_e}} + \frac{\psi}{\text{Re}_p^n} \left(A_{\text{True}} \exp \left[\frac{-E_{A,\text{true}}}{RT} \right] \right)^{1/2} \quad (12)$$

By defining a new parameter as (Eq. 13):

$$\kappa = \frac{1}{\frac{3}{(d_p/2)} \sqrt{D_e} A_{\text{True}}} \quad (13)$$

Eq. 12, which expresses the global kinetic rate as a function of flow behavior and temperature, becomes Eq. 14:

$$\frac{1}{k_{\text{obs}}} = \frac{\kappa}{\exp \left[\frac{-E_{A,\text{true}}}{2RT} \right]} + \frac{\psi}{\text{Re}_p^n} \quad (14)$$

Based on Eq. 14, **TABLE 1** summarizes the effect of flow behavior and temperature on the individual rate controlling step. Note that, as revealed in **FIG. 3**, the exponential effect of pore diffusion rate control is typically represented by an apparent activation energy, which is half of the true intrinsic value.

Estimating catalyst performance in a commercial fixed-bed reactor.

To successfully scale up from a laboratory and pilot reactor to a commercial scale, the global kinetic correlation (Eq. 14) must be experimentally determined. First, Eq. 14 is transformed to a linear form by taking the natural logarithm of both sides. If the experimental conditions (mainly reaction temperature) are chosen, such that the film diffusion is the rate-limiting step, then Eq. 3 is valid. By varying the Re_p^n (proportional to fluid velocity), the value of ψ can be obtained from the slope of **FIG. 2**.

Next, experimental conditions (mainly using sufficiently small catalyst pellet size at relatively low temperature and high fluid velocity) are chosen, such that the surface reaction rate is the rate-limiting step, the true intrinsic activation energy $E_{A,\text{true}}$ can be estimated from a plot

TABLE 1. Effect of flow behavior and temperature on each individual rate-controlling step

Rate-controlling step	Flow behavior	Temperature
Film diffusion	Re^n	~ Linear
Pore diffusion	Independent	Exponential
Intrinsic	Independent	Exponential

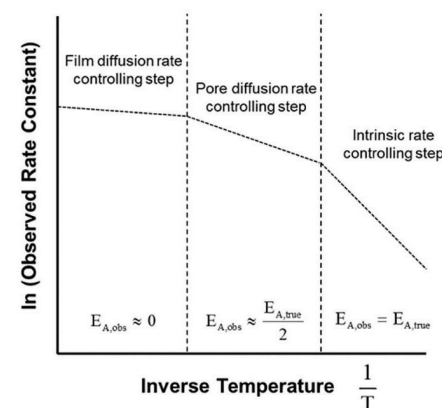


FIG. 3. Effect of temperature on the observed global rate constant, as well as the region of each rate-limiting step.³

similar to FIG. 3. Finally, experiments are carried out at sufficiently high fluid velocity so that the last term of Eq. 14 may be ignored. By varying reaction temperature T , a plot similar to FIG. 3 can be used to obtain the value of κ from the slope and the earlier obtained value of $E_{A,true}$. In this way, the handy correlation (Eq. 14) for the non-isothermal reactor can be determined. An example is given in Eq. 15.

Case study. Consider the case of a gas-phase, fixed-bed reactor involving the production of olefins from an isomerization reaction using a typically porous catalyst. The reaction is mildly exothermic and the proprietary catalyst was tested extensively in three different scales (laboratory, pilot and demonstration units) using the above-mentioned variety of experimental conditions. The obtained correlation is shown in Eq. 15:

$$\frac{1}{k_{obs}} = \frac{0.0234}{\exp\left[\frac{-165,250}{2RT}\right]} + \frac{1.192 \times 10^7}{Re_p^{0.5}} \quad (15)$$

TABLE 2 compares the experimental and predicted % conversion for the four scales of the fixed-bed reactor. Obviously, the correlation was reasonably accurate for the laboratory, pilot and demonstration reactors. Though the actual conversion data for the commercial unit is unavailable, the predicted conversion is expected to be quite satisfactory.

Takeaway. The unsuspected shift of the rate-controlling step is a common pitfall during comprehensive new process/product development, beginning from catalyst development and testing at labo-

ratory and pilot scales to the up-scaled design and adiabatic operation of the commercial unit. The most effective approach is to “begin with the end in mind.” More specifically, a viable commercial unit should be conceptually designed as soon as basic catalyst performance data in laboratory scale has been obtained.

To make the commercial unit viable (technically and economically feasible), the necessary and essential targets of catalyst performance and improvement can be reasonably determined. These scientific targets are valuable preliminary requirements for the catalyst developer to satisfy before more extensive catalyst testing is carried out in the laboratory and subsequent pilot scales. To enhance the successful design and operation of the commercial reactor with mass throughput by operating in adiabatic (non-isothermal) mode and turbulent flow regime, the most scientifically sound approach is to develop a handy practical correlation similar to Eq. 14, which can handle exothermic/endothermic reactions taking place using catalyst of optimal pellet size and shape. Of course, the crucial issue of catalyst stability and deactivation must also be addressed adequately and the requirements incorporated into the above catalyst performance targets. Note: Although the present contents are based on the assumption of irreversible first-order reaction, the same or at least a similar methodology is applicable to more complex reaction types and pathways. **HP**

LITERATURE CITED

- Levenspiel, O., *Chemical reaction engineering*, 3rd Ed., John Wiley & Sons, New York, New York, 1998.
- Worstell, J., *Adiabatic fixed-bed reactors practical guides in chemical engineering*, 1st Ed., Elsevier, 2014.

³ Fogler, H. S., *Element of chemical reaction engineering*, 5th Ed., Prentice Hall, Upper Saddle River, New Jersey, 2016.

NOMENCLATURE

a_p	Cross-sectional area of the pore, m^2
A_{obs}	Observed or apparent pre-exponential factor, s^{-1}
A_{true}	True pre-exponential factor, s^{-1}
$E_{A,obs}$	Observed or apparent activation energy, J/mol-K
$E_{A,true}$	True activation energy, J/mol-K
C_{As}	Concentration of A at the surface of catalyst, mol/ m^3
d_p	Catalyst particle diameter, m
D_e	Effective diffusivity, m^2/sec
k_{obs}	Observed overall rate constant, s^{-1}
k_{PD}	Mass transfer rate constant within the catalyst pore, m/sec
k_{intr}	Intrinsic reaction rate constant, s^{-1}
k_{ED}	Mass transfer rate constant within at fluid-solid film, m/sec
κ	Characteristic constant
n	Characteristic constant/reaction order
η	Effectiveness factor, dimensionless
R	Gas constant
Re_p	Packed-bed Reynolds number, dimensionless
S_c	Exterior surface area of the catalyst particle, m^2
T	Temperature, K
v_p	Average pore volume, m^3
V_c	Catalyst pellet volume, m^3
ψ	Characteristic constant.



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TABLE 2. Comparison of actual and predicted catalyst performance from reactor model in four different scales of reactors

Parameters	Laboratory	Pilot plant	Demonstration	Commercial
Diameter, mm	15	21	66	3,000
L/d_p	59	266	1,087	2,048
Mass throughput range	g/hr	g/hr	kg/hr	metric t/hr
Catalyst particle, mm	~2	~2	~2	~2
Feed type	Real feed	Real feed	Real feed	Real feed
Operation	Isothermal	Isothermal	Isothermal	Adiabatic
Catalyst used	g-scale	g-scale	kg-scale	ton-scale
Flow behavior	Laminar	Transition	Turbulent	Turbulent
% conversion: expected/predicted	79/72	77/78	72/71	.../74

Management of LPG pool in a complex refinery

LPG pool management is becoming more important as the regulations on the product specifications tighten. If this pool is managed unwisely, it can lead to throughput reduction or even unit shutdown.

At Tüpraş' İzmit refinery, LPG is produced in three crude distillation units (CDUs), one fluid catalytic cracking unit (FCCU), one delayed coking unit (DCU), two Platformers, one diesel hydrotreating unit (DHTU) and two hydrocracking units (HCUs). Some of these LPG products are sent directly to storage tanks, while others require posttreatment. Three LPG treaters help meet sulfur-based specifications, and a C₃/C₄ splitter is followed by a selective hydrogenation unit (SHU) to meet butadiene specifications. Additionally, an LPG recovery compressor with a chiller and an LPG evaporator is used, according to production planning requirements.

Eight production/sales spherical tanks and three bullet tanks for off-specification LPG product are managed without interrupting production and sales activities. Storage tanks are connected to one another, to jetties and to customer pipelines for sales and loading/unloading activities.

The aim of this article is to define how to manage a complex LPG pool of 10 sources with different specifications for purity, butadiene content, total sulfur and evaporation residue. Ways of coping with different pool challenges due to upsets and unit shutdowns are described.

LPG product specifications. Automotive gas and LPG are comprised of propane, propylene, butane, butane isomers, butene and traces of other hydrocarbons.¹ Product specifications for automotive gas and LPG are defined according to EN-589 directives. Limitations are defined for motor octane number (MON); total dienes content including 1,3 butadiene; hydrogen sulfide (H₂S); total sulfur content after odorization; copper strip corrosion; evaporation residue; vapor pressure gauge at 40°C; vapor pressure gauge at minimum 150 kPa at five temperature grades; water content; and odor (**TABLE 1**).

In 2019, the EN-589 automotive gas and LPG specification was revised to incorporate a maximum 1,3 butadiene content of 0.1 m/m. The specification for propane content was proposed to be changed from a volume basis to a mass basis, to be applied in two steps: first 20% and then 30%. However, consensus was not achieved on 30% propane content, so this revision was postponed for further evaluation. A final change for the LPG specification is maximum total sulfur content, which was decreased from 50 mg/kg to 30 mg/kg.

LPG pool. The general configuration of LPG production at the İzmit refinery is shown in **FIG. 1**. LPG from the DCU, FCCU, CDU1, CDU2 and CDU3 are rich in H₂S and mercaptans. They must be treated in LPG Merox units (Merox 1, Merox 2 and Merox 3). The DCU LPG can be treated in both Merox 1 and Merox 3. The DCU and FCCU LPG products are rich in butadiene content. The butadiene-containing, sulfur-treated LPG from Merox 1 and Merox 3 are sent to a downstream unit—a combination of a C₃/C₄ splitter and a selective hydrogenation unit (SHU)—to meet butadiene specifications. After passing through the C₃/C₄ splitter, the C₃ and C₄ can be stored separately.

The rest of the LPG produced in Platformer 1, Platformer 2, the DHP, HCU1 and HCU2 normally does not require LPG

TABLE 1. LPG specifications¹

Property	Limits		Test method
	Minimum	Maximum	
MON	89		Annex B
Total dienes content, %m/m		0.5	EN 27941 DIN 51619
1,3 butadiene, %m/m		0.1	DIN 51619
Propane content from April 1, 2021 will be evaluated, %m/m	20 30		EN 27941 DIN 51619
H ₂ S	Negative		EN ISO 8819
Total sulfur content (after odorization), mg/kg		30	EN 17178 ASTM D6667
Copper strip corrosion, (hr at 40°C), rating	Class 1		EN ISO 6251
Evaporation residue, mg/kg		60	EN 15470 EN 15471 EN 16423
Vapor pressure gauge at 40°C, kPa		1,550	EN ISO 4256 EN ISO 8973 and Annex C
Vapor pressure gauge at minimum 150 kPa at five temperature grades:			EN ISO 8973 and Annex C
Grade A, °C		-10	
Grade B, °C		-5	
Grade C, °C		0	
Grade D, °C		10	
Grade E, °C		20	
Water content	Pass		EN 15469
Odor	Unpleasant and distinctive at 20% LFL		See 6.3 and Annex A

Merox treatment, as these units have individual treatment sections and the LPG is sent directly to storage. An extra connection exists between the DHP LPG product and the deethanizer to increase the purity of the DHP LPG product, which in turn increases the purity of the LPG pool. HCU1 LPG can be sent to storage either after the debutanizer or after the debutanizer plus the deethanizer.

The LPG recovery compressor, which incorporates a chiller and an LPG evaporator, affects the LPG pool and rundown routing. Additionally, off-spec LPG from storage can be re-treated in Merox 1 and Merox 2. Since these units can treat only sulfur components, only H₂S, total sulfur and corrosion strip specifications can be manipulated directly.

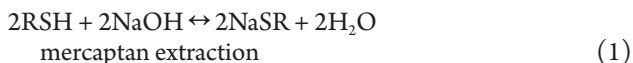
LPG processes. The following sections detail the units used in the LPG process.

Merox units. The LPG Merox units are used to remove residual H₂S and mercaptan sulfur (RSH-S) compounds from LPG products. The LPG product is sent to the Merox units after amine treating to decrease the H₂S content.

A typical Merox unit consists of prewash and extraction sections, where LPG product is treated with caustic; and a caustic regeneration section, where caustic is regenerated in the presence of catalyst and air for reuse.

The caustic concentration is different in the prewash and extraction sections to treat H₂S and mercaptan compounds selectively. LPG is first pretreated in the prewash section with 10°Baumé caustic for H₂S removal and then routed to the extraction section, where mercaptan-rich LPG is mixed counter-currently with 20°Baumé caustic solution in a trayed tower. During mixing, mercaptans are transferred from the LPG to the caustic solution.

The reactions for the process are shown in Eqs. 1 and 2:



LPG product is posttreated by moving it through the settler and sand filter after extraction. Regenerated caustic is used until it is spent and then sent to the caustic neutralization unit before disposal.

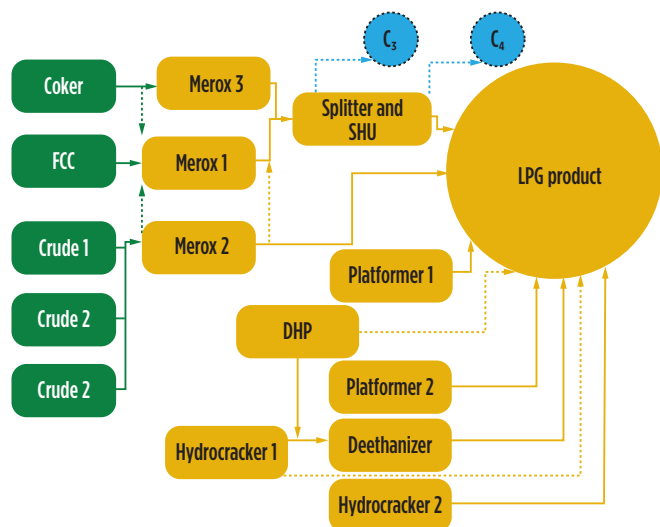


FIG. 1. LPG pool configuration at the İzmit refinery.

posal. The circulation rate of regenerated caustic is important, as mercaptan removal increases as the circulation rate increases, but disulfide content coming from the caustic also increases and affects total sulfur. For this reason, an optimum rate should be used.

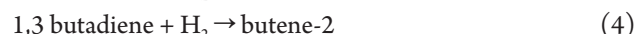
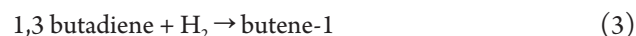
LPG inlet temperature, caustic temperature, caustic concentration, caustic spent rate, caustic/hydrocarbon rate, amount of oxidation air and catalyst affect LPG product treatment efficiency (FIG. 2).

The İzmit refinery has three LPG treater units. Two are traditional Merox units (Merox 1 and Merox 2). The common practice is to treat crude unit LPG products in one unit and butadiene-rich FCCU and DCU LPG products in the other unit. The two Merox units are connected to each other, so routing different products to the other treater or common usage of some sections are allowed. In case of a sulfur- or corrosion-related problem in any of the LPG producing units, the product can be routed to the LPG treaters before being sent to storage. During startup or shutdown of the LPG units, the product can be routed to treaters or off-spec tanks. A naphtha wash system was added to Merox 1 and Merox 2 to increase sulfur removal.

The Merox 3 unit is used to treat only DCU LPG product.

Selective hydrogenation unit. The selective hydrogenation process (SHP) is the hydrogenation of C₄ to mono-olefins over a highly selective, fixed-bed catalyst. Various palladium and nickel-based catalysts are used for SHP reactions. These catalysts are affected by contaminants including carbon monoxide, total chloride, H₂S, carbonyl sulfide, nitrogen, metals, caustic, water and total sulfur.³ Selective hydrogenation catalyst loading is carried out by either sock loading or dense loading. Selective hydrogenation reactions are controlled by pressure, temperature, liquid hourly space velocity (LHSV), hydrogen addition rate and effluent recycle ratio.

The SHP reactions are shown in Eqs. 3 and 4:



In refineries, feed is supplied from the C₄ cut of the FCCU LPG and the DCU LPG. At the İzmit refinery, there is an additional feed option from storage. FCCU LPG and DCU LPG are first separated in a C₃/C₄ splitter, and butadiene-rich C₄ is sent to the SHP unit feed drum. Butadiene-rich C₄ is pressurized to define the reaction pressure by means of feed pumps and is optionally connected by the reactor recycle effluent. This combined feed is heated to reaction temperature and is combined with H₂. The combined feed is sent to the reactor, where reactions occur in the liquid phase. Light ends and excess H₂ of the reactor effluent are separated and sent to the fuel gas system. The saturated C₄ product is cooled and sent to product storage either directly or in combination with C₃ from the C₃/C₄ splitter.

Offgas compressor and working modes. The main purpose of the offgas compressor is to recover LPG from clean gases and increase the LPG amount. Six clean gas sources feed the offgas compressor from the overheads and the DEA absorbers. These gases are pressurized in two stages, and low-purity LPG is recovered. Since the purity of this LPG is around 70%, it is not directly sent to the rundown tank or directed to the deethanizer or debutanizers.

FIG. 3 shows the two compressor modes: (A) deethanizer first, and (B) debutanizer first. In the deethanizer-first mode,

low-purity LPG is recovered from the offgas compressor and sent directly to the deethanizer to remove the C_2 - components. Then, C_2 - free LPG is sent to the debutanizers to decrease the C_5 + components. Four debutanizer options are incorporated in this network: CDU, DHP, Platformer and FCCU. According to the free capacities of each debutanizer column, the LPG coming from the deethanizer is shared among these debutanizers.

To use the deethanizer-first mode, all sources to the deethanizer (except the offgas compressor outlet) should be removed. This usually has a negative effect on pool purity. The deethanizer-first mode is generally preferred in summer, as the gas loads of the columns are higher due to hot weather. In this way, the additional LPG load routed to the debutanizers is decreased.

In the debutanizer-first mode, low-purity LPG is shared in the debutanizers of the CDU, DHP, Platformer and FCCUs. Then, LPG from the DHP debutanizer can be sent to the deethanizer, since the DHP debutanizer has lower purity.

The amount of recovered LPG from the offgas compressor can be further increased with the use of a chiller compressor by decreasing the temperature after the second stage of the compressor. By using the chiller compressor, the purity of the recovered LPG is relatively increased.

Evaporator. A controlled process according to production planning instructions or product quality is the evaporation unit. Only one low-pressure steam evaporator is directly connected to the Merox 1 product line; therefore, the required low-sulfur LPG product is evaporated to the fuel gas ring in the refinery. As the fuel gas increases by evaporation, the consumption of natural gas as fuel is decreased.

In general, LPG from the FCCU is treated in the Merox 1 unit. Therefore, the use of an evaporator unit has a negative effect on LPG product purity and a positive effect on the butadiene content of the LPG. If there is any limitation on LPG purity, some LPG product can be directed to the Merox 1 unit; however, there is no need for Merox treatment of the LPG content that will be vaporized.

Startup and product routing. During startup, it is always best to direct rundown to off-spec tanks since operating conditions are not yet stabilized. Sending a rundown of unknown quality to the product pool is risky; it can cause all products to

go out of specification, as well as blockage of storage, lack of storage capacity, lack of product and customer complaints. In addition, upsets may occur during startup, which may result in product with a different composition from a typical LPG. Especially in the earlier stages of startup, product flowrates are not stabilized and can experience drastic fluctuations, which can cause problems in the downstream units.

When operation parameters are stabilized for LPG, composition/purity (IP-405), copper strip corrosion (IP-411), sulfur compounds (ASTM-D-5504) and dissolved residues (EN 15470) analyses should be carried out for rundown. If composition and purity are close to normal values, copper strip corrosion is 1, H_2S is 0 and evaporation residue is less than 60 mg/kg for rundown, then the product can be directed to the refinery LPG pool.

General problems and troubleshooting. The following sections explain some general issues encountered in LPG processing and how to troubleshoot them.

High sulfur content. As explained previously, the sulfur content of the LPG product is removed by Merox units after being treated by the amine absorber columns. Some units have

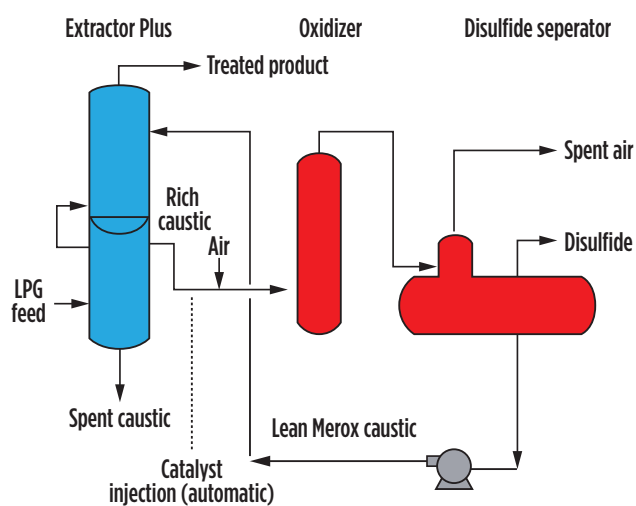


FIG. 2. LPG Merox process flow diagram.²

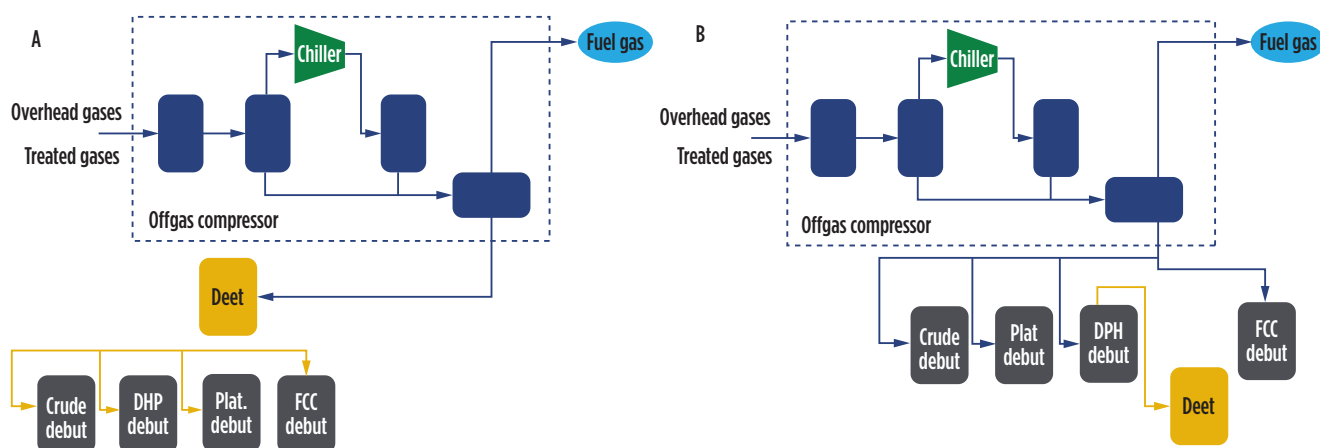


FIG. 3. Offgas compressor configuration modes: (A) deethanizer first, and (B) debutanizer first.

their own caustic treatment sections, and the rest send their products to the Merox units. In the LPG pool, if a unit has an LPG product with high mercaptan or H_2S content, then its product is routed to the Merox units to treat the product further. This problem may arise from bad caustic quality or high caustic spent rate of these units.

While the product is routed to the Merox units, necessary actions are taken in those units to achieve required product quality. An alternative solution is routing the product to off-spec tanks and then processing in Merox units with desired flowrates. This solution can be applied if the Merox unit feedrate is near the design limit, and it is advantageous because the extra flowrate, rather than the entire stream, can be processed in a Merox unit.

In Merox units, high sulfur in the LPG product should be analyzed from different perspectives. Caustic quality, operating parameters and feed properties affect the efficiency of Merox units. First, the sulfur type should be examined as a key for how to solve the problem. Mercaptans, disulfides, H_2S and others that may come from crude oil or cracking units (e.g., thiosulfate) are common examples. Ethyl and methyl mercaptans can be treated more easily in Merox units. When the chain becomes longer, treatment becomes more difficult. If the cause of high sulfur is dimethyl sulfide, then the caustic circulation rate should be checked. A high circulation rate may increase “re-entry sulfur,” which causes high sulfur in the product. Naphtha or kerosene wash systems may be implemented to treat re-entry sulfur.

Another common issue is caustic quality. Caustic quality and the spent rate should be checked, and if these parameters are over the limits, then the caustic should be replenished. Prewash and regenerated caustic inventory have different percentage spent limits. Among the operating parameters, feed temperature and caustic temperature affect extraction efficiency heavily, while air injection rate and catalyst quality and amount affect the oxidation process. Air injection may cause corrosion problems in the lines and equipment, so it should be observed closely.

In a large LPG pool with many sources, even if the sulfur content of some LPG products increases, it does not necessarily put the pool in jeopardy. This effect may be diluted with the help of the entire LPG pool. Even if an LPG tank is out of specification due to a high sulfur parameter, blending with other LPG tanks may be enough to overcome the issue, depending on the sulfur level.

On the other hand, if high-sulfur-containing LPG is routed to the SHU, then the catalyst may be affected badly. Its efficiency may decrease, and recovery of the catalyst may take some time, depending on the sulfur level it is exposed to and the capability of the catalyst against sulfur. This may lead to another problem: butadiene. To avoid this problem, if an LPG stream that is being treated by the SHU experiences a high-sulfur situation, then it is removed from the SHU, and the unit may need to be taken into circulation in case of low throughput.

Butadiene. The FCCU and DCU are the sources of butadiene in the İzmit refinery LPG pool. If all the units are operating near design values, then this butadiene content is diluted in the pool and remains within limits. If the pool becomes too narrow due to upsets or planned shutdowns, then the butadiene content may go off-spec.

Normally, the SHU combined with a C_3/C_4 splitter is used to decrease butadiene content by changing dienes into butenes. If a

performance issue is experienced in the SHU or if the catalyst is in an end-of-run state, then removing some of the C_4 s from the LPG pool may be necessary. By removing C_4 , butadiene is also decreased. This C_4 stream is taken from the splitter C_4 outlet and used in the gasoline pool. The amount of C_4 is limited by the control valve range, as well as line and tank metallurgy, as removing so much C_4 from the system causes the C_3 ratio to increase, and vapor pressure approaches design limits. In addition, it is not possible to add C_4 s to the gasoline pool in summer due to dry vapor pressure equivalent (DVPE) specifications.

If a market option is available, then selling these C_4 s may also be evaluated. A second option is to route the LPG product with high butadiene content to the evaporator. In this way, high-butadiene-containing LPG is evaporated and used in the fuel gas system. This method is useful when natural gas prices are high, as the fuel gas system is normally supported by natural gas.

Another option is to increase the amount of LPG that does not contain butadiene in the pool as a way of diluting butadiene. For this purpose, the offgas compressor may be used and the net gas of the isomerization unit may be routed to the Platformer unit to gain LPG. A final option is to adjust the DCU and FCCU parameters to decrease their LPG product or their butadiene content. The decreasing riser temperature of the FCCU also decreases the amount of LPG product. However, low riser temperature has the disadvantage of octane loss. Also, decreasing wash oil (naphtha) circulation in the absorbers of the DCU gas plant decreases butadiene content by leaving some C_4 s to the fuel gas stream.

Purity. Some units have high purity in their LPG products like the FCCU, DCU or new HCU, which may go as high as 100%, while some old units like the CDU or the diesel desulfurization unit (MQD)/Platformer have a purity of 95% or lower. If high-purity LPG is lost due to an upset or planned shutdown, then the pool purity may be in jeopardy.

In such a case, the first option is to check all the debutanizer columns and make necessary parameter changes to increase purity. This may take some time, as it may be necessary to perform purity tests to determine the problematic debutanizer column, if the temperature and pressure profiles do not provide enough information to troubleshoot. In addition, it is necessary to determine if the cause of low purity is C_2- or C_5+ . Once determined, the debutanizer top temperature, pressure or reboiler duty are adjusted accordingly.

A second option is to activate the deethanizer column. This column increases the purity by removing the C_2- content of the product. The İzmit refinery has one deethanizer column, which has a capacity sufficient for only the LPG products of the old HCU and the MQD.

A third option is to open the pressure control valves in the Merox units' LPG feed drums to shift some of the C_2- content to the fuel gas system. This action has a limited effect and has the disadvantage of increasing H_2S content in the fuel gas system, since LPG Merox feed may contain some amount of H_2S .

A final option is to increase the high-purity LPG and/or to decrease the low-purity LPG in the system. Decreasing the low-purity LPG may be achieved by routing this stream to the evaporator; the pros and cons of this action was previously discussed. The net gas stream may be routed to the fuel gas system from the Platformer debutanizer column, which produces relatively low-purity LPG. The deethanizer and debutanizer modes

of the offgas compressor also affect LPG product purity.

Corrosion. A copper strip corrosion test (FIG. 4) is a visual and subjective test. Some results may appear very close to one another, which may require repeat testing on some occasions. Corrosion problems in LPG product generally arise from H_2S content and usually occur due to bad caustic quality or high caustic spent rate. On rare occasions, the issue stems from the amine treating section. A problem in the amine system may bring high H_2S load to the caustic system, which may prevent the desired zero H_2S in the product.

Actions to be taken for corrosion problems are similar to those taken for a high-sulfur problem. LPG product with a corrosion problem is routed to a Merox unit for further treatment, and the caustic inventory of the unit is investigated and replenished during this period. Off-spec tanks may be used initially; however, if the Merox unit is near its design throughput, then the product with corrosion is treated in the Merox unit to the fullest capacity.

In some units like the new HCU, H_2S analyzers enable observation of the problem at the beginning. This is important since, unlike sulfur problems, blending is not a solution when an LPG tank is subject to corrosion. It cannot be diluted enough to achieve zero-corrosion product. Also, the risk remains of the problem spreading to the other LPG tanks.

Evaporation residue. Evaporation residue can easily arise from a dirty sample bottle or lab equipment, or from a hydrocarbon leak from the amine system or any of the units. The residue may change from a dirt particle into a hydrocarbon droplet. In a complex pool, it may be one of the most difficult problems to diagnose. A hydrocarbon leak from the process systems to the amine system may create this issue and cause danger for the pool, as the amine regeneration section may not be capable of cleaning the system in a short time. Filters in those units, LPG sample containers and lab equipment should be checked for dirt, oil and other potential contaminants.

Another constraint is the test method for residue. The evaporation residue test is a long process that may take up to 7 hr, and it is not very sensitive. As time is important for protecting the LPG pool, product with the residue problem should be routed to off-spec tanks or a spare product tank. This will create space and time for detecting the cause of the problem and finding the best solution while not spoiling the product tank.

Merox units and caustic treatment systems cannot treat evaporation residue. Blending the off-spec tank or processing the product in an off-spec tank with low flowrates may be seen as options, but if the residue amount is high, then it may not be possible to solve the issue by blending the tanks and processing the off-spec product, as this will take a very long time.

If the cause of residue is hydrocarbon and the amount is so high that it is not feasible to blend the tanks or process the product, then the best way to treat evaporation residue is to route the off-spec product to the debutanizers for reprocessing. This may not be an option for many refineries, as extensive lines are necessary among product tanks and units to enable sending off-spec LPG to debutanizers. However, this method allows for eradication of C_{10} – C_{40} from the LPG product.⁵

In the İzmit refinery, a large amount of off-spec LPG product caused by a process upset was routed to debutanizers from storage tanks and reprocessed in just two weeks using this method. Normally, it would take months to process this LPG

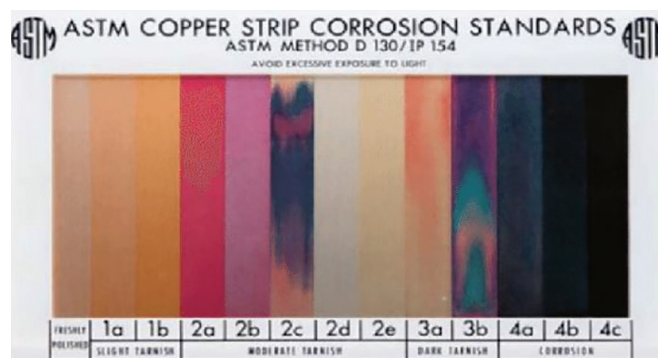


FIG. 4. ASTM copper strip corrosion chart.⁴

in Merox units or blend the tanks, which would create inventory cost and cause difficulties in production planning due to blocked LPG tanks.

Takeaway. A complex refinery may have many sources of problems in its LPG pool, as well as solution alternatives. It is important to correctly diagnose the problem and the source of the problem, and then choose the best alternative solution. The biggest constraint is time, and the biggest concern is the probability of having an off-spec pool. In 2020, through close observation and unit cooperation, the on-spec tank ratio was maintained at approximately 99% in the İzmit refinery. LPG pool complexity may create problems, but it can also offer solutions.

Propane specification was not elaborated in this article, as uncertainties exist on the issue. However, according to LPG product composition, additional needs may help supply the necessary propane level in the pool. The option of selling C_4 to market or importing C_3 can be analyzed. Additionally, using excess C_4 in the fuel gas system or in hydrogen production units may be examined. Most of these options create the need for new equipment, such as C_3 / C_4 splitters, evaporators or even storage tanks that are suitable for propane. **HP**

LITERATURE CITED

- ¹ BSI, "BS EN 589:2018: Automotive fuels: LPG: Requirements and test methods," December 2018.
- ² ESC, "Pengerang energy complex: Environmental impact assessment," April 2019, Johor, Malaysia, online: https://enviro2.doe.gov.my/ekmc/wp-content/uploads/2019/05/J18-780_PEC_Chapter-5-Project-Description.pdf
- ³ "Fuels selective hydrogenation process," General operating manual.
- ⁴ Gao, S., L. Yang, B. Deng and J. Zhang, "Corrosion mechanism for local enrichment of acids and copper ions in copper-insulating paper contacts leading to the acceleration of copper sulfide formation induced by dibenzyl disulfide," *RSC Advances*, Vol. 7, Iss. 83, November 2017.
- ⁵ Van Raalte, W., "It's all about the residue," *The Analytical Scientist*, January 14, 2013, online: <https://theanalyticalscientist.com/techniques-tools/its-all-about-the-residue>

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External pressure design of large-diameter piping: Optimal analysis approach

Large-diameter piping used in the petrochemical, oil and gas, steel plant and power industries often carry toxic fluids and can pose significant safety hazards. Their stability and reliability are important while they operate under external pressure loading due to vacuum formation or any other external load that can potentially collapse the piping system.

Major piping codes, such as the ASME B31 pressure piping series¹, refer pressure vessel codes for the design of piping subjected to external pressure. However, piping and pressure vessel configurations are usually different, and a pressure vessel external pressure design approach should be carefully considered when applied to piping. In the author's experience, a design by rule (DBR) approach as stipulated in various pressure vessel codes is conservative in nature; those rules are conservatively applied to a specific piping system without due consideration of its actual geometry, pipe support location and configuration. However, these aspects have considerable impact on the external allowable pressure/loading capacity of a piping system.

However, a design by analysis (DBA) approach can address this issue effectively, considering the actual layout of the piping and support location/configuration and even optimizing the piping wall thickness requirement while meeting allowable external pressure loading criteria. This article briefly compares the various rules and approaches of the external pressure design per various international codes and intends to help practicing engineers to adopt a suitable approach for specific applications to optimize design within current pressure vessel code framework.

RULES, PROCEDURES AND PRINCIPLES

Classical approach for infinity long shell. External pressure causes compressive stress in piping or pressure vessels, creating stability problems and potentially leading to failure. Large-diameter and thin pipes are more susceptible under external pressure than thicker pipe; however, even thick piping may also be subjected to failure where external pressure is significant, such as in a subsea environment.

Bresse-Byran offered an allowable external pressure design formula² with a factor of safety (FOS) of 3 considering two lobes for an un-stiffened portion of piping (Eq. 1):

$$P_{allow} = \frac{2Es}{3(1-\nu_s^2)} \left(\frac{t}{D_0^3} \right) \quad (1)$$

Another commonly used formula (Eq. 2) for above-ground steel pipe from AWWA M-11³ is often used by engineers working on a water main of steel construction. This formula is from the original Timoshenko equation⁴ (without an FOS) for an unreinforced, infinite length:

$$P_c = \frac{2Es}{(1-\nu_s^2)} \left(\frac{t}{D_0^3} \right) \quad (2)$$

DBR approach for pressure vessel codes. DBRs on external pressure design are outlined in various international codes, such as ASME Boiler and Pressure Vessel Code (B & PVC) Section VIII, Div. 1, UG-28 to UG-30, and B & PVC Section VIII, Div. 2, EN-13445/PD 5500.^{5,6} However, these code rules are primarily meant for tubular structure design under only external pressure loading, but are not applicable for combined additional loading, such as axial compression or bending.

ASME B&PVC Code case 2286,⁷ first published in 1990 and reaffirmed in the 2004 edition, was intended to address the combined loading of compression and external pressure applied to a tubular structure. The 2286 code case is applicable to both Div. 1 and Div. 2 vessels and was later merged into the main code of Div. 2.

However, the methodologies and conservatism associated with each code related to external pressure design are different. ASME B & PVC Section VIII, Div. 2 offers both DBR and DBA in Parts. IV and V, respectively. B & PVC Section VIII, Div. 1 (UG-28 to UG-30) DBR is a little conservative in approach but still preferred and widely used for piping/pressure vessel design, as these calculations are less time-consuming and more straightforward.

DBA approach for pressure vessel codes. In 2007, new code rules were introduced in ASME B & PVC Section VIII, Div. 2, and the DBA approach was included under the ASME B & PVC rewrite program. The DBA approach offers a rigorous method of analyzing pressure vessel/piping engineering problems using a numerical method.

The buckling analysis due to external pressure as well as other loading can be analyzed by three primary methods per the DBA approach, as defined in Part V of the Div. 2 code in a compressive stress field:

1. Linear buckling (Eigen value buckling) analysis, or Type 1 analysis (FIG. 1)
2. Non-linear buckling analysis with effect of non-linear geometry/material, or Type 2 analysis
3. Non-linear collapse analysis with geometry/material non-linearity considering shell imperfection, or Type 3 analysis.

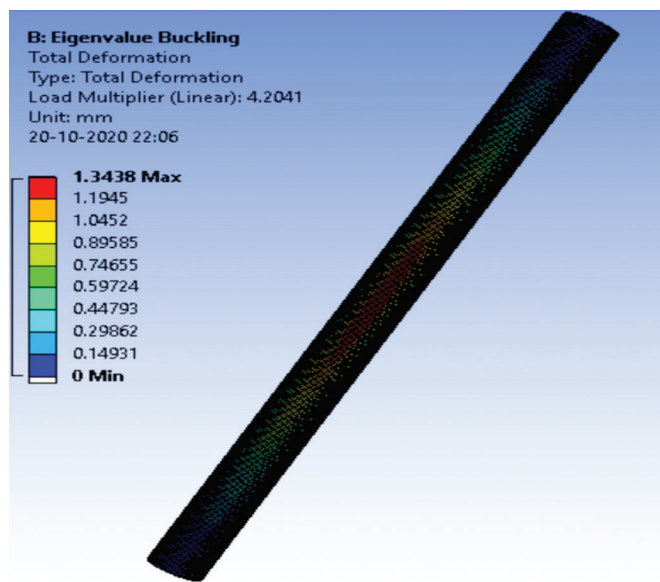


FIG. 1. FEA result with first Eigen mode of buckling with load multiplier (LM) 4.2.

TABLE 1. Geometry and material data (SS 316 at 21°C) for sample calculation

Geometry parameter

Outer diameter of shell (un-stiffened), mm	2,130
Shell wall thickness, mm	20
Shell support to support distance, m	10–60

Material parameter¹²

Elastic modulus (Es) (psi)	28.3E6
Poisson ration (ν_s)	0.3

In general, Type 1 analysis results in the greatest overestimate of collapse load, so the largest design margin is used. Type 2 analysis results in a lower estimate in the buckling load and a lower design margin is used. Type 3 analysis results are the best estimate for collapse load as both material and geometric nonlinearity, along with shell imperfection, are included in numerical analysis and no capacity reduction factors are used.^{8,9} However, no discussion or analysis results have been produced on Type 3 buckling analysis in this article.

In the European pressure vessel code EN 13445, two approaches exist to DBA. One is the so-called direct approach, while the other is historically older and is referred to as the elastic stress categorizations approach. Both have different merits according to the complexity of the design. However, detailed discussion related to external pressure design DBA application per EN 13445 is outside the scope of this work.

SAMPLE COMPARATIVE STUDY ACROSS PRESSURE VESSEL CODES

This section compares the different code-allowable external pressures of large diameter piping, with TABLE 1 showing the properties for the varied magnitude of an un-stiffened length (support-to-support length).

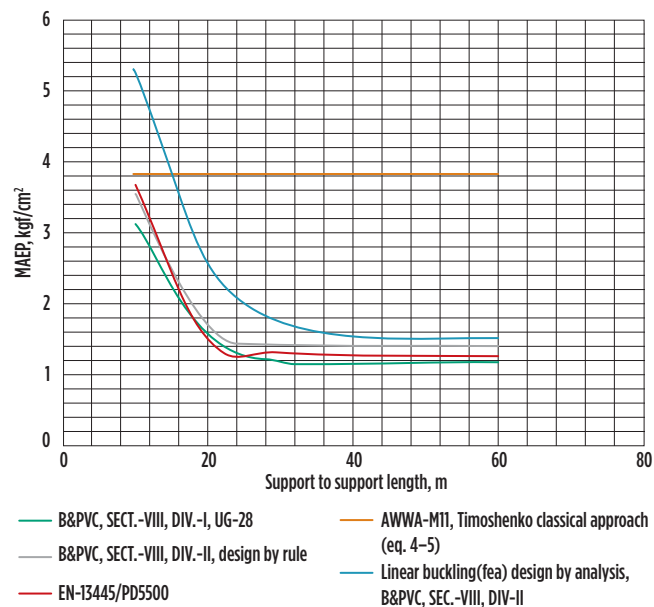


FIG. 2. MAEP plot per various pressure vessel codes vs. support-to-support length.

TABLE 2. MAEP result data per various pressure vessel codes

Support-to-support length, m	B & PVC, Section VIII, Div. 1, UG-28 (kgf/cm ²)	B & PVC, Section VIII, Div. 2, DBR (kgf/cm ²)	EN-13445/PD5500 (kgf/cm ²)	AWWA-M11, Timoshenko approach, Eqs. 4 and 5	Linear buckling (FEA) DBA, B & PVC, Section VIII, Div. 2 (kgf/cm ²)
10	3.13	3.54	3.69	3.82	5.3
20	1.56	1.7	1.48	3.82	2.61
30	1.19	1.42	1.31	3.82	1.73
40	1.19	1.42	1.28	3.82	1.56
50	1.19	1.42	1.27	3.82	1.51
60	1.19	1.42	1.27	3.82	1.51

For a sample study, an un-stiffened cylindrical shell with 20-mm wall thickness of material of construction 316 grade SS was considered. The varied support-to-support length and maximum allowable external pressure (MAEP) capabilities have been determined as per various codes to obtain the trend of conservativeness across the pressure vessel codes on an external pressure design approach.

Assumed data for MAEP study and result table/plot.

TABLE 2 represents the MAEP per various pressure vessel codes vs. the varied support-to-support length. **FIG. 2** shows the plot of the same data.

The MAEP, as tabulated/plotted here, was calculated based on DBRs of various pressure vessel codes and other standards, such as AWWA M11. Additionally, the MAEP based on the DBA approach per ASME B & PVC Section VIII, Div. 2, Part V was calculated using the procedure below and compared with the DBR result set.

FIG. 3 represents a finite element model result of a linear buckling analysis with a support-to-support length of 30 m (with a 2,130-mm diameter SS 316 shell with 20-mm thickness at 21°C) and with the same properties shown in **TABLE 1**.

Therefore (Eq. 3):¹⁰

$$\begin{aligned} \text{MAEP [3]} &= \frac{\text{Applied external pressure} \times \text{load multiplier (LM)}}{\text{design factor } \Phi_B \text{ (per part.-V, div-ii)}} \\ &= \frac{1.03 \times 4.20}{2.5} = 1.73 \text{ kgf/cm}^2 \end{aligned} \quad (3)$$

where,

$$\Phi_B = 2/\beta_{CR} = 2/0.80 = 2.5$$

$$\beta_{CR} = 0.8 \text{ for external pressure on the shell.}$$

Similarly, for a varied support-to-support length starting from 10 m to 60 m, the result was tabulated in the sixth column (from left) of **TABLE 2**.

Observations/discussion on comparative study. ASME B & PVC Section VIII, Div. 2 DBR for external pressure design¹⁰ is the most conservative, followed by EN-13445/PD-5500 and B & PVC Section VIII, Div. 2 design by rules per the data and plot shown in **TABLE 2** and **FIG. 2**.

Also in **TABLE 2** and **FIG. 2**, DBA (linear buckling, Type 1) per ASME B & PVC Section VIII, Div. 2, Part V⁸ provides a non-conservative result for certain support-to-support length based on the outer diameter of the pipe (in this case, 2,130 mm), after which the result converges and the MAEP is almost independent of support-to-support length.

The AWWA – M11/Timoshenko formula (without an FOS) is basically an overestimate of the MAEP compared to other code rules and does not include the effect of support-to-support length.

DBA: Type 1 linear buckling of actual piping configuration/layout with restrained condition. **FIG. 3** represents

a piping FEA buckling result under external pressure from one piece of equipment to another (anchor-to-anchor), with the properties shown in **TABLE 1**. A linear buckling analysis (Type 1) was performed to evaluate the allowable external pressure, as per the DBA approach of ASME B & PVC, Section VIII, Div. 2, Part V.

Piping model properties. The piping model properties have been kept the same as **TABLE 1** except that the configuration/layout was considered per **FIG. 3** with the length of each leg as 10 m, a total developed length of 30 m, and a restraint boundary condition where both ends are fixed (equipment end). Result summary: For the linear Type 1 buckling analysis, Eq. 4 is used:

$$\begin{aligned} \text{MAEP} &= \frac{\text{Applied external pressure} \times \text{load multiplier (LM)}}{\text{design factor } \Phi_B \text{ (per sect.-V, B \& PVC, div-ii)}} \\ &= \frac{1.03 \times 11.90}{2.5} = 4.90 \text{ kgf/cm}^2 \end{aligned} \quad (4)$$

where,

$$\Phi_B = 2/\beta_{CR} = 2/0.80 = 2.5$$

$$\beta_{CR} = 0.8 \text{ for the external pressure on the shell.}$$

DBA Type 2 non-linear buckling analysis of actual piping configuration with restrained condition. A non-linear Type 2 buckling analysis was performed on the same piping configuration as **FIG. 3** as per Part V of B & PVC, Div. 2.⁸ **FIG. 4** represents the non-linear FEA result plot, and the inset figure shows the load factor plot for non-linear time step analysis. Result summary: For the non-linear Type 2 buckling analysis¹¹, Eq. 5 is used:

$$\begin{aligned} \text{MAEP} &= \frac{\text{Applied external pressure} \times \text{Load factor}}{\text{design factor } \Phi_B \text{ (per sect.-V, div-ii)}} \\ &= \frac{15.29 \times 0.7}{2.08} = 5.14 \text{ kgf/cm}^2 \end{aligned} \quad (5)$$

where,

$$\Phi_B = 1.667/\beta_{CR} = 1.667/0.8 = 2.08$$

$$\beta_{CR} = \text{the effect of shell imperfection} = 0.8 \text{ for external pressure on the shell.}$$

DBA Type 1 and Type 2 analysis results comparison. **TABLE 3** represents the summary of the buckling analysis results from Sections IV and V for actual piping configuration/layout with restrained condition.

One intriguing observation is that the non-linear Type 2 analysis MAEP without the design factor stipulated by the Div. 2 code is slightly less than that of the linear Type 1 (10.70 kgf/cm² vs. 12.25 kgf/cm²). However, for this particular application, the final MAEP for the Type 2 analysis is greater than Type 1 due to a significant difference in design factor for these two types of analysis.^{12,13,14,15}

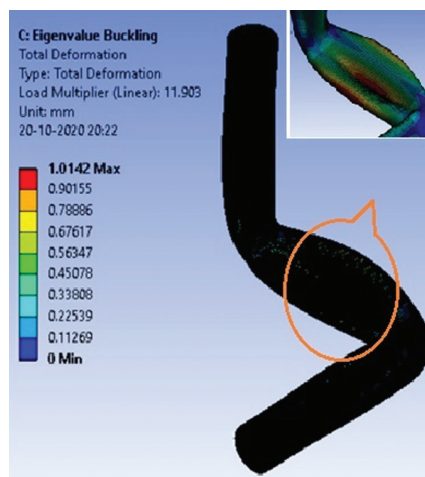


FIG. 3. FEA result with first Eigen mode of buckling with LM 11.90. Inset figure shows the buckled shape of the shell at the first buckling mode.

DBA linear and non-linear method adopting analysis approach. While Type 2 and Type 3 non-linear buckling analyses are more realistic and non-conservative methods compared to the linear elastic Type 1 analysis, they require a significant amount of engineering effort and data related to geometric and material imperfection. In particular, Type 3 analysis—which considers both geometric and material non-linearity as well as shell imperfections—is the least conservative. However, it is complex and requires significant computational effort, making it an unrealistic approach for regular engineering applications.

A Type 1 linear elastic buckling analysis is straightforward with comparatively lesser computational efforts. However, it produces a less conservative result than compared to pressure vessel code design by rule methods (DBR), leading to significant design optimization and material cost savings.

Takeaway. Pipe wall thickness estimation and fixing the stiffener/support location for external pressure loading through the DBR of pressure vessel codes is easy to apply and has been a traditional approach for many years for large-diameter piping design. These rules are conservative and, in many cases, can result in overdesign of the system. In case of multiple loading, such as axial compression and bending and an external pressure loading scenario, these rules are not applicable to predict buckling.

However, for costly material and more critical applications, provisions within the code (e.g., the DBA approach) provide rigorous engineering analysis and, therefore, more optimized solutions with significant material savings. Additionally, the DBA approach is suitable to predict buckling in multiple loading scenarios.

Once the DBA approach is adopted for buckling analysis for external pressure design, an FEA model can be built with the

actual layout of the piping system with exact restraint/support locations. The location of the stiffener can also be fixed based on the buckling mode shapes to obtain an optimized solution.

With applications of the FEA method gaining popularity among piping and pressure vessel engineering industries, DBA methods have become more relevant than ever. For critical applications involving expensive material and in-service scenarios, the material/geometric non-linearity effect can be accounted for and fitness for service can be ascertained through Type 2 or Type 3 buckling analysis—or even the simpler Type 1 analysis—for a new design, providing a more realistic result than the traditional code DBR approach. **HP**

ABBREVIATIONS:

DBR	Design by rules
DBA	Design by analysis
B & PVC	Boiler and Pressure Vessel Code
LM	Load multiplier
MAEP	Maximum allowable external pressure
FOS	Factor of safety
BC	Boundary condition
FEA	Finite element analysis
E_s	Modulus of elasticity
D_0	Shell diameter
t	Shell wall thickness
ν_s	Poisson ratio
P_{allow}	Allowable external pressure
P_c	Collapsing pressure
β_{CR}	Shell imperfection effect, B & PVC, Section VIII, Div. 2, Part V
ϕ_B	Design factor, B & PVC, Section VIII, Div. 2, Part V

LITERATURE CITED

- American Society of Mechanical Engineers, ASME B31.3, "Process Piping," 2018.
- Peng, L.-C. and T.-L. Peng, *Pipe stress engineering*, American Society of Mechanical Engineers (ASME), 2009.
- ANSI/AWWA Standard M11, *Steel—A guide for design and installation*, American Water Works Association, 2016.
- Timoshenko, S. P., *Theory of elastic stability*, 2nd Ed., McGraw-Hill, 1985.
- BS EN-13445, "Unfired pressure vessel," Part 3, 2018.
- BS PD 5500, "Specification for unfired fusion welded pressure vessels," 2018.
- American Society of Mechanical Engineers (ASME), Code Case 2286-1, "Alternative rules for determining allowable external pressure and compressive stresses for cylinders, cones, spheres and formed heads," Section VIII, Div. 1 and 2, Cases of the ASME Boiler & Pressure Vessel Code, 2001.
- American Society of Mechanical Engineers (ASME), "ASME Boiler & Pressure Vessel Code," Section VIII, Div. 2, 2019.
- American Society of Mechanical Engineers (ASME), PTB-1, "Criteria and commentary," Section VIII, Div. 2, 2014.
- American Society of Mechanical Engineers (ASME), "ASME boiler and pressure vessel code," Section VIII, Div. 1, 2019.
- DNV, DNVGL-RP-C208, "Determination of structural capacity by non-linear finite element analysis methods—Recommended practice," 2019.
- American Society of Mechanical Engineers (ASME), "ASME boiler and pressure vessel code," Section II, 2019.
- Miller, C. D. and K. Mokhtarian, "Proposed rules for determining allowable compressive stresses for cylinders, cones, spheres and formed heads," Welding Research Council Bulletin 406, New York, 1995.
- Miller, C. D., "Commentary on the alternative rules for determining allowable compressive stresses for cylinders, cones, spheres and formed heads for Section VIII, Div. 1 and 2," Welding Research Council Bulletin 462, New York, 2001.
- American Society of Mechanical Engineers (ASME), Section VIII, Div. 2, Example Problem Manual, PTB-3, 2013.

TABLE 3. Buckling analysis result for actual piping configuration/layout with restrained condition

Type of analysis	MAEP without code safety design factor (kgf/cm ²)	Code safety design factor (ϕ_B)	MAEP with design factor (kgf/cm ²)
Type 1, linear	12.25	2.5	4.9
Type 2, non-linear	10.7	2.08	5.14

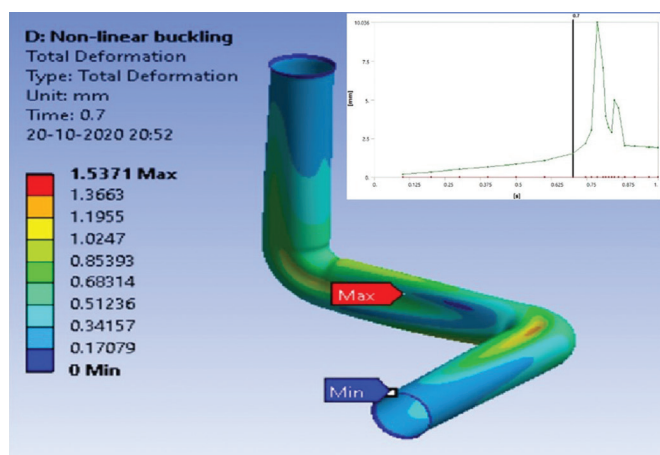


FIG. 4. Nonlinear FEA collapse pressure profile. The inset figure shows a time-step analysis with a load factor of 0.7).



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Implementation of advanced level control techniques in refinery operations

Plant performance depends on stable operations, with steady feed, product flow, temperature and pressure control as per process requirements. Plant performance can be improved further by stabilizing column and vessel levels through suitable level control techniques. The residue fluid catalytic cracking unit (RFCCU) is one of the most important secondary processing units to increase refining margins. RFCCU margins depend on uninterrupted operations and the best possible product yield. This is accomplished by keeping unit severity steady and maintaining the fractionation of product without quality giveaways or failures. Any identified deviation from stable operations (e.g., temperature, pressure, flow indication and control valve operation) should be corrected.

A refinery generates a significant amount of sour water from its process units, such as the crude distillation unit (CDU), vacuum distillation unit (VDU), RFCCU and delayed coking unit (DCU), among others. Oil carryover, along with sour water, are common problems in the refinery. The DCU generates a lot of sour water due to its tedious batch processes, which can include coking, stripping, coke cooling and coke cutting. An adequate control system for sour water separation and disposal will help to reduce oil carryover, along with sour water.

The removal of hydrogen sulfide (H_2S) from the product stream and recycle gas is imperative before routing the finished product to the rundown vessel/tank and before routing recycle gas for further use. H_2S must also be removed from generated fuel gas (FG) prior to being used in the firing furnace.

Brief description of the RFCCU. The RFCCU has two sections: a reaction section and a product fractionation section. In the reaction section, vacuum gasoil (VGO) feed is cracked in the presence of circulating catalysts. Reactor vapor enters the fractionator column. After cooling, the overhead vapor accumulates in the overhead vessel. Part of the liquid returns to the top of the column as reflux for maintaining the required temperature and for balancing material pump-out to the gas concentration unit (GCU). Vapor coming out from the top of the overhead vessel is compressed through a wet-gas compressor and routed to the GCU after cooling. Product drawn from the middle of the fractionator is light cycle oil (LCO), which is routed to the diesel pool through a stripper to remove lighter materials from the product. Slurry oil—also known as

clarified oil (CLO)—is drawn from the bottom of the fractionator column and routed to the DCU feed or the internal fuel oil system.

Analysis of product draw and level control. The fractionation-section LCO product draw and the bottom-section level control both play critical roles. In RFCCU operations, some catalyst fines travel in reactor vapor and settle in the bottom section of the fractionator column. To remove catalyst fines from the bottom of the column, a minimum slurry flow must be maintained. It was observed that reducing LCO product was required to maintain slurry flow.

To evaluate column bottom and LCO levels, analyses were conducted to monitor trends in level, valve opening and flow. Major bottom level control and flow deviations were observed. Level,



FIG. 1. RFCCU bottom level, C/V opening and slurry r/d flow trends before and after TON control.

flow and control valve opening trends for the bottom product are shown in the top section of **FIG. 1**. Due to the bottom rundown flow variation, other critical operating parameters were observed, such as the variation in the slurry recycle flow and preheat temperature and a slight fluctuation in the reactor outlet temperature. Due to the variation in reactor temperatures, a slight reduction in conversion was noticed, resulting in a reduction in LCO yield.

Implementation of target opening nonlinear (TON) control. As bottom level and slurry flow variations were marginally high in the PID control system, it was decided to implement TON control for performance improvement of bottom level control. TON control is a correlation-based control, and it works based on the differences of set level and actual level. The correlation used for level control is shown in Eq. 1:

$$CV_{OP} = (L_A - L_S) * M + T_{OP} \quad (1)$$

The calculated output to the bottom rundown flow control valve (CV_{OP}) = [Actual bottom level (L_A) – set level (L_S)] \times M + target output (T_{OP}).

Control configuration can be selected as:

1. Normal distributed control system (DCS) mode
2. TON control mode.

This modification can be carried out in the DCS, with the help of an instru-

ment engineer. Apart from the selection of DCS or TON, three fields exist in the DCS: target output, level set point and factor M . Target output is the average opening of the bottom level flow control valve. The level set point is the desired bottom level to be maintained. The actual level indication value will be taken from the DCS. M is a factor to be set once as per operating practice and flow variation with level, which is very similar to controller gain. It will usually vary from 1–2.5.

Benefits. After implementing TON control, the bottom level and flow controller performances were found to be highly encouraging. The performance trend after implementation is shown in the bottom section of **FIG. 1**. After implementing bottom level monitoring with TON control, the other bottom circuit flow (e.g., slurry recycle to the reactor, bottom pumparound and quench flow) became stable due to a steady slurry draw rate. After implementing TON control, LCO dropping to the bottom was eliminated due to steady slurry rundown flow. This resulted in a steady reactor outlet temperature and an improvement in conversion, with a reduction in slurry yield of 0.5%–1%.

Based on RFCCU bottom level performance and experience, a similar TON control was implemented in the VGO mild hydrocracking unit (MHCU) bottom level control. Bottom level control was in level controller/flow controller (LC/FC) cascade control, with run-

down flow to the tank. The problems were level and flow variations in a cyclic pattern due to the inherent character of PID control, and the maximization of hot feed was limited due to the rundown flow variation. TON control was implemented, providing a 10%–12% increase in hot feed to the RFCCU.

Brief description of DCU coke drum operation.

Coke drum changeover in the DCU is a normal process. After completion of the coking cycle, the coke drum switchover takes place. After isolation of the coke drum, there are two operational steps before coke cutting: stripping for the removal of H/C from the coke drum and cooling of the coke. During stripping, steam is introduced from the bottom of the coke drum, followed by process water for cooling. Blowdown material from the coke drum is routed to the blowdown tower, where tower overhead material is collected in an overhead receiver vessel after cooling. The receiver vessel has two separate compartments with level indication (i.e., for hydrocarbon and sour water). Hydrocarbon is pumped to the blowdown column for quenching, and sour water is pumped to the sour-water stripper (SWS) unit for further treatment. There are two pumps: one is for hydrocarbon pumping, and the other is for sour water pumping. As coke drum switchover is a batch operation, both sour water and hydrocarbon pumps will operate (start/stop) based on minimum and maximum set level indications.

Analysis of operation. Oil carryover and sour water were occasionally at elevated levels due to the pump running at maximum capacity, along with frequent starts and stops of the pump. To avoid frequent starts and stops, one control valve was provided for the sour water pumping system, with the objective of reducing oil carryover and sour water. Sour water level control was done in LC control mode with the new control valve. After installation of the control valve, oil carryover and sour water were reduced but could not be eliminated due to the continuous fluctuation of sour water flow. Fluctuation in sour water generation was 15 m³/hr–400 m³/hr. The level and flow fluctuation are shown in the top section of **FIG. 2**.

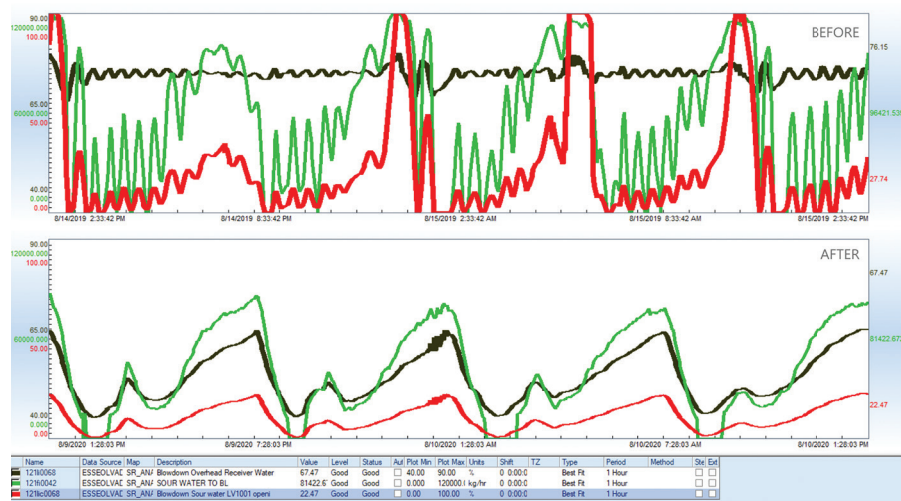


FIG. 2. DCU blowdown vessel interface level, C/V opening and flow trends before and after TON control.

Implementation of TON control. The system was working better after the installation of the control valve. However, oil carryover continued. To improve operations, TON control was implemented for sour water interface level control. This simple modification was configured in the DCS, and the system's performance is now highly encouraging and satisfactory.

Benefits. After implementing TON control, a drastic reduction in oil carryover, along with sour water, was noticed. An additional advantage of TON control is that flow increases based on the level difference—hence, additional separation volume for higher flow. A reduction in sour water flow variation resulted in less level variation in the SWS surge vessel level. The blowdown receiver sour water level, control valve opening and flow trend (24-hr operation) are provided in the bottom section of FIG. 2.

Brief description of the amine regeneration unit (ARU). The ARU plays a critical role to maintain product quality, especially for the removal of H₂S from products like LPG and FG. The ARU supplies regenerated lean amine to the DCU, the FCCU and the CDU/VDU amine scrubber. Similarly, rich amine is sent to the ARU from the amine scrubber (i.e., DCU LPG and FG, FCCU FG, CDU LPG and FG, and VDU offgas). Rich amine accumulates in a surge vessel for the removal of hydrocarbons, if any. It is then routed to a stripper for the removal of H₂S. The stripper bottom's temperature is maintained by the steam reboiler. Overhead acid gas from the regenerator (H₂S with water vapor and other gases) is cooled through an air and water cooler, and then routed to the overhead vessel. Acid gas from the overhead vessel is routed to the sulfur recovery unit (SRU). A differential pressure indication across the column is provided to understand amine carryover, along with the gas and performance of the amine stripper.

Analysis of operation. The system operates in a steady manner; however, sudden increases of differential pressure across the column can sometimes be observed. This is an indication of amine carryover, along with acid gas, resulting in a disturbance in the SRU. On analy-

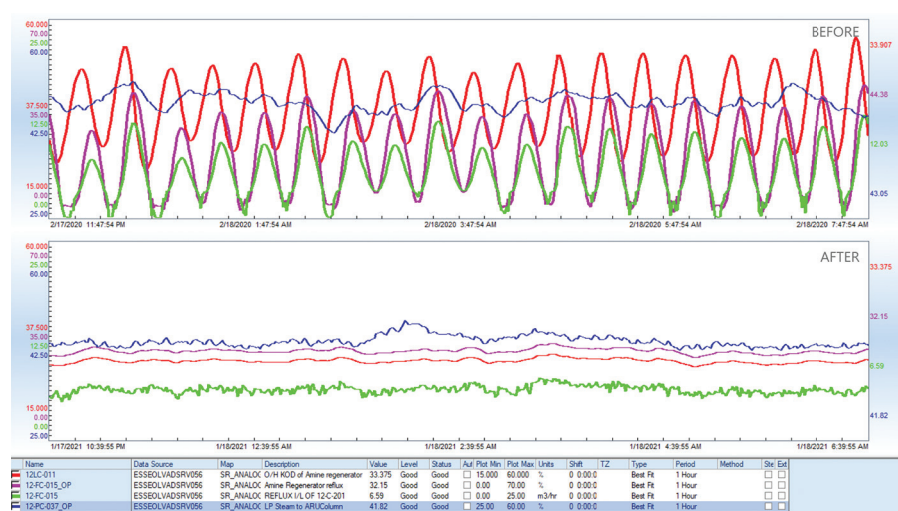


FIG. 3. ARU overhead vessel level, flow, control valve opening and reboiler steam flow trends before and after TON control.

sis of the ARU overhead vessel level, flow and opening trends, a fluctuation was noticed with the reboiler steam flow control valve. The overhead level, flow and control valve opening trends are shown in the top section of FIG. 3. Based on these observations, TON control logic was implemented. The performance after implementation of TON control is shown in the bottom section of FIG. 3.

Benefits. Steady overhead level control resulted in a steady acid gas flow to the SRU and the elimination of abnormal and/or sudden increases in differential pressure across the column. The column temperature and pressure are steady due to steady reboiler steam flow and top reflux flow, which improves amine regeneration.

Approximately 60% of the rich amine comes from the DCU FG scrubber and LPG scrubber, and the gas generation rate fluctuates by 12%–15% during coke drum changeover. It was observed that the incoming rich amine flow to the ARU was varying to some extent and that the combined flush vessel provided for FG and LPG scrubber level control was not working properly. TON control was implemented for the FG scrubber and flush vessel level control. Both are working satisfactorily in auto control mode, and rich amine flow variation was reduced.

Based on one ARU's performance, two more ARUs in the refinery—used for supplying amine to hydroprocessing units and to catalytic reforming units (CRUs) and SRUs—have implemented

TON control for overhead vessel level control.

Takeaway. Refinery units like the RFCCU and the VGO MHCU are crucial for optimization of refinery performance and maximization of profitability. Stable operations of these units will help to increase refining margins. Additionally, stable operations of the sour water vessel level will reduce oil carryover and sour water, which will improve SWS unit performance. Improved performance of the ARU will increase H₂S removal from rich amine and H₂S recovery from FG, LPG and recycled gas will increase. TON control has been implemented in the RFCCU and VGO MHCU bottom levels; three ARU overhead levels; the DCU FG amine scrubber and flash vessel levels; and the DCU blowdown overhead sour water level control at Nayara Energy Ltd.'s refinery in Vadinar, Gujarat, India. All are working exceptionally well on a continuous basis. **HP**



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Corrosion under insulation on stainless steel

Corrosion under insulation (CUI) is a severe form of localized external corrosion that occurs on stainless steel (SS) that has been insulated. It is a costly problem in the process, chemical and pharmaceutical industries, with millions of dollars spent on inspection and repair of equipment over the past several years.

Although CUI is common in carbon steel, it also affects SS, which is otherwise considered corrosion resistant. This corrosion manifests in the form of severe pitting. The main reasons for CUI occurrence in SS are the presence of chlorides and fluoride ions in insulation, the presence of an electrolyte (mainly water) and the presence of oxygen. Sometimes, the presence of acids gives rise to accelerated acid corrosion, which is not discussed in this article.

Furthermore, metal temperatures in the range of 50°C–175°C are prone to external stress corrosion cracking (ESCC) failures under these circumstances.

Relevant standards and test methodologies. A number of standards define the requirements for thermal insulation that is to be used in contact with SS. However, only ASTM C795, the standard specification for thermal insulation for use in contact with austenitic SS, is considered for this article.

ASTM C795 references two other test methods, ASTM C692 and ASTM C871. **FIG. 1** from ASTM C795 shows the reference standard for determining the chemical acceptability of the insulation material. It indicates the acceptability of insulation material on the basis of the plot points of Cl + F and Na + SiO₃ analyses. Tests must be conducted in accordance with ASTM C692 and ASTM C871.

ASTM C692, the standard test method for evaluating the influence of ther-

mal insulations on ESCC tendency of austenitic SS (otherwise known as the “28-d coupon test”) is a test method that evaluates the corrosion possibility of insulation in contact with stressed SS coupons. In this test, water is wicked through insulation or dripped onto non-wicking insulation that is in contact with the SS coupons. After a period of 28 d, the SS coupons are examined for any signs of ESCC. Four coupons must be tested to comply with the requirements of the standard, and none of them can show ESCC. If any of the coupons show cracking, then the insulation has failed the test.

ASTM C871, the standard test method for chemical analysis of thermal insulation materials for leachable chloride, fluoride, silicate and sodium ions, is the

test method for determining leachable chloride, fluoride, silicates and sodium ions in an insulation. The results from this test are checked with the empirical graph in **FIG. 1** in ASTM C795 for “chemical acceptability” for use on SS, which is determined if the plot points of these analyses fall within the acceptable area of **FIG. 1**.

For an insulation material to be acceptable for use in contact with SS, the material must meet the chemical acceptability criteria and pass the 28-d coupon test. Passing only one of the two tests is not sufficient.

Pre- and post-insulation considerations. Once the insulation material selection is finalized, there are several important considerations for pre-insulation

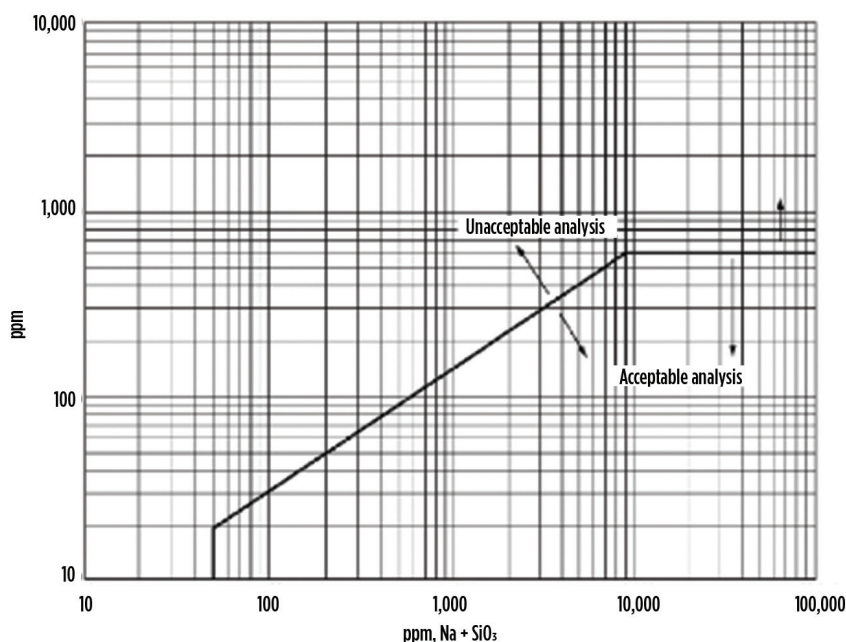


FIG. 1. Acceptability of insulation material on the basis of the plot points of Cl + F and Na + SiO₃ analyses. Figure: ASTM C795: Standard specification for thermal insulation for use in contact with austenitic SS (2018).

laying activities and regular monitoring post-insulation to minimize CUI on SS.

Pre-insulation laying activities include:

1. Hiring an insulation contractor of good reputation is an important step to avoid CUI problems. Before laying the insulation, ensuring a selection of good-quality vapor barrier mastic, glass cloth fabric, foam sealer and SS jacketing is vital for achieving a leakproof arrangement and eliminating the ingress of rainwater or moisture into the insulation material.
2. Insulation material lots received at the site are often dumped into a corner without adequate storage to prevent moisture ingress. Such practices must be strictly avoided. ASTM C390, the standard practice for sampling and acceptance of thermal insulation lots, provides helpful insight in this regard.
3. Insulation of equipment and piping should be carried out at the site after installation. If the insulation is carried out at a vendor shop for some reason, it must be ensured that there is no possibility of water/moisture ingress during transportation. A detailed procedure must be prepared and approved by a competent authority prior to shipping. This is specifically important when the insulated equipment/piping is transported through a sea route, as the sea atmosphere is high in moisture and salt laden, which can have detrimental effects on insulation material during transportation.
4. Some standards suggest the use of aluminum over the metal surface prior to laying insulation to shed water; however, it should be noted that aluminum is a potential fire hazard due to its low melting point. The use of aluminum should be avoided in fire hazard zones.
5. Some specifications recommend the application of paints prior to laying insulation; however, the effectiveness of this procedure must be checked with the insulation material specialist for the intended use.

Regular monitoring post-insulation activities include:

1. An insulated surface always looks acceptable from the outside. This may give a false impression, as the surface below the insulation could be encountering CUI, which can go unnoticed for a considerable period of time.
2. All the low points under insulation in vertical equipment, such as dish heads, bottoms of horizontal vessels, individual nozzle low points, nozzle interfaces, piping low points, areas near supports, etc., must be regularly monitored for corrosion. These low points typically show signs of CUI, as the moisture/water generally drips down to these areas due to gravity. A portion of the insulation can be opened up for inspection. In case of doubt, the previously mentioned tests can be repeated to ascertain any signs of CUI.
3. Upon opening the affected area, if any pitting is observed on the surface, then loss of thickness must be assessed for fitness-for-service (FFS) of pressure equipment using standards such as API 579-1/ASME FFS-1. Based on the results of the assessment, it should be decided whether or not the equipment should be put back in service.
4. A periodic inspection schedule should be in place to check the insulated surfaces for any sign of CUI or leakage.

CUI on SS may not be eliminated completely; however, it can be reduced to a great extent using the approaches outlined in this article. **HP**



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Monitor ppb monomer impurities and catalyst poisons with process GC-MS

Competition in the ethylene market is fierce and demands for the quality of the ethylene are increasing. High-purity monomers are used to make polyethylene and polypropylene, the polymeric building blocks for two important plastics. Numerous potential ethylene impurities reduce the quality and value of ethylene by interfering with the subsequent production costs of polyethylene. Non-ethylene hydrocarbons can result in non-ethylene polymers being produced. Contaminants such as oxygenates, sulfurs and metal hydrides like arsine and phosphine have significant impacts on the metallocene catalyst required to produce polyethylene.

For example, the catalyst is poisoned by even trace levels of common byproducts, such as hydrogen sulfide (H_2S), acid gases and methanol (CH_3OH). This poisoning reduces catalyst efficiency, resulting in lower polymer yields per reaction. Catalyst bed poisoning also necessitates increased maintenance events and associated plant downtime, and, eventually, significant catalyst replacement costs. For these reasons, polyethylene producers demand high-purity ethylene. Careful monitoring of ethylene process streams is required for early detection and remediation of contaminants to meet product specifications.

Analysis. The oxygenates, hydrocarbons, permanent gases and sulfurs potentially found in monomer streams are very different compound classes and require multiple detector types for their complete analysis. Classic process gas chromatographs (PGCs) frequently house a single

detector type that necessitates multiple instruments to address the complete analyte list. Laboratory GCs routinely use temperature-programmable convection ovens and capillary chromatography to achieve excellent analyte separation and resultant low sensitivities.

In contrast, most PGCs are limited to isothermal air-bath ovens and use packed columns, resulting in poorer detection limits for analytes of interest. It should be noted that the metal hydrides arsine and phosphine, which are potent catalyst poisons, are not addressable by typical PGCs. Therefore, for the hydrides, or for low-ppb (parts per billion) quantitation of other process stream compounds, offline analysis is required.

Offline analysis poses several challenges for analysis of process streams, the riskiest of which is time. The additional time required to take a manual “grab” sample back to the lab increases the risk that changes in the process might affect product quality before action can be taken. The chemical composition of the sample is also at risk and might not reflect the true composition of the process stream. For example, light components can volatilize out of the sample and be lost in the head space of the sampling container. Reactive components can be lost on the surface of the sampling container. The precision of the PGC measurements is often greater than that of laboratory measurements because there are fewer changes to the sample and increased automation reduces measurement variation.

However, laboratory analysis does offer at least two benefits. Critical pro-

cesses often have analytical redundancy to safeguard against loss of data in the event of instrument downtime and lab instruments often fulfill this role. Lab GCs have also been relied on to offer advanced methods and additional detector choices, such as mass spectrometers (MSDs), not included in typical PGCs.

MSDs are nearly universal and very sensitive detectors capable of quantifying analytes in the ppb range. Except for hydrogen and helium, an MSD can detect all analytes of interest. MSDs have a broad dynamic range (10^6) that allows them to be maximally useful in the plant where concentration ranges can vary considerably. The troubleshooting advantages of a mass spectrometer are unparalleled and allow for interrogation of “mystery” peaks, or alternatively, “the usual suspects” that show up from time to time in a process stream. Both types of anomalies are easily addressable by an MSD. Finally, as will be discussed in greater detail here, GC-MSD can offer triple verification of the identity of an analyte. To the best of the authors’ knowledge, no other PGC has offered GC-MS as an option.

The objective in the design of this instrument was to create a PGC capable of lab-quality performance to address the full list of impurities of interest in ethylene and propylene streams. To achieve that goal, temperature-programmed capillary chromatography was combined with GC-MSD, GC-PDHID (pulsed discharge ionization detector) and GC-FID (flame ionization detector). Complete characterization of the C_1 – C_{5+} hydrocarbons, permanent gases, common sulfurs and

oxygenates, arsine and phosphine in an ethylene stream was achieved in 10 min.

Basics of GC-MS. An in-depth review of GC-MS is beyond the scope of this paper and a basic understanding will be adequate for the purpose of this discussion.

GCs—using capillary columns carefully chosen for the chemical properties of their surface coating—spatially resolve analytes within a sample by virtue of the variable interaction of those analytes with the column coating. As the separated

compounds elute from the column, they are directed to a detector for quantitation.

As the name suggests, the mass analyzer of a quadrupole mass spectrometer uses the mass of a molecule for identification and the abundance of that mass for quantitation. There are several important steps of this process, outlined in [FIG. 1](#).¹

Compounds within the GC column eluates are delivered to the inlet of the MSD where they are exposed to electrons released by a heated filament. This interaction does two things. First, the electrons bombard the molecule and fragment it in a structure-dependent fashion—the unique chemical structure of the molecule dictates the way the molecule will break apart under electron bombardment. This fragmentation pattern, as well as the relative abundance of the different fragments, is unique to the molecule. The impact of the electrons also strips an electron from the intact molecule and its frag-

ments confer a charge on them.

The charged intact molecules (called molecular or parent ions) and fragments (called fragment or daughter ions) are accelerated and guided through the instrument by a tunable, DC and RF electric field in the quadrupole mass analyzer.² This field functions as a filter by allowing only selected ions, which resonate with the field, to make it to the detector while non-resonant ions are deflected away. It is the mass-to-charge ratio (m/z) that is selected but, because the charge is 1, the ion mass is readily determined. The selected ions then strike an electron multiplier, which greatly amplifies the signal and sends it to the data system for quantification.

The observed m/z , the mass spectra, for methanol and diethyl sulfide are shown in [FIG. 2](#). These unique compounds have distinct spectra with characteristic peaks. Methanol has a parent m/z at 32 and a dominant fragment m/z at 31. Diethyl sulfide has a parent m/z at 90 and a dominant fragment m/z at 75. The fragmentation patterns, as well as the ratios of the abundances of the fragments, are constant and defining for these molecules. This allows for unambiguous identification of methanol and diethyl sulfide.

The importance of this fact is highlighted in [FIG. 3](#). Methanol and diethyl sulfide often co-elute and are observed as a composite peak, seen at 8.84 min in this example ([FIG. 3A](#)). With an MSD, this composite peak can be separated by examining extracted ion chromatograms (EICs), which are individual chromatograms for a desired m/z ([FIG. 3B](#), diethyl sulfide and [3C](#), methanol). As expected, the retention time of the individually extracted and resolved compounds matches that of the composite peak. EICs allow for quantitation of each individual contributor to the composite peak and clearly demonstrates one of the greatest advantages of the MSD.

MSDs also allow for the identification of unknown peaks that might appear in a chromatogram. The analyzer can be configured to identify the mass (m/z) of the peak, which can then be found in a mass spec library. Alternatively, if the presence of a specific compound is suspected, the indicative masses (m/z) for this analyte can be quickly added to the analyte list to determine if the compound is present. Subsequent analysis of a prepared sample can be confirmatory and quantitative.

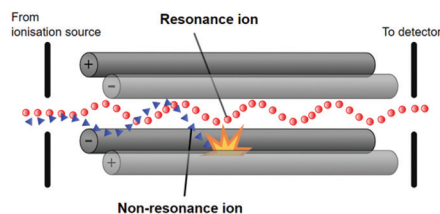


FIG. 1. Quadrupole mass analyzer.¹

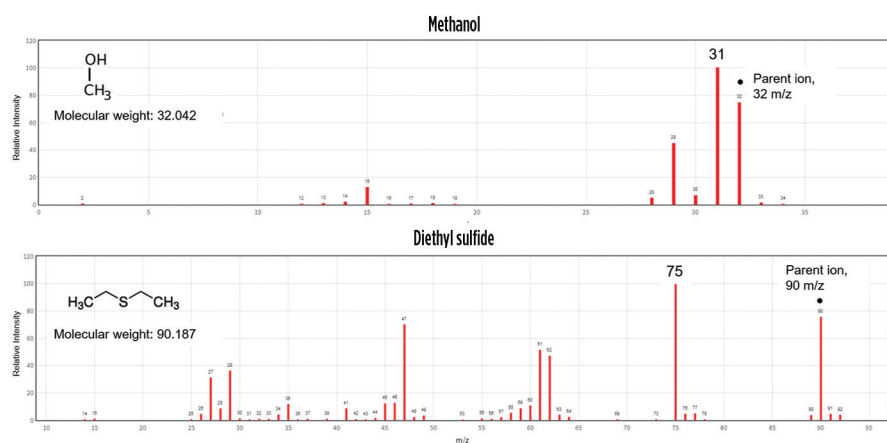


FIG. 2. Example of mass spectra: methanol (top) and diethyl sulfide (bottom) have unique mass spectra. Source: NIST Chemistry WebBook, SRD 69.

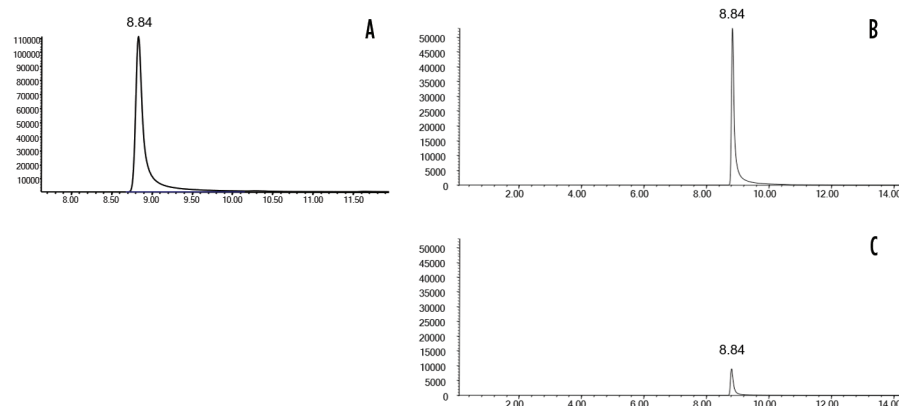


FIG. 3. Extracted ion chromatograms resolve co-eluting compounds: (A) chromatogram showing co-elution of diethyl sulfide and methanol at 8.84 min; (B) EIC of diethyl sulfide; and (C) EIC of methanol.

Lastly, GC-MSD can offer triple confirmation of an analyte by agreement of the expected retention time, correctness of the spectrum of the molecular and fragment ions, and the coincidence of those ions in the extracted ion chromatograms at the expected retention time.

Case study: Instrument design. The process GC monomer analyzer^a (FIG. 4) used in this study was designed and built by the authors' company. It was designed for one of the largest petrochemical companies in North America to speciate C₁–C₄ hydrocarbons and numerous common catalyst poisons (H₂S, COS, methyl mercaptan, ethyl mercaptan, methanol, arsine and phosphine) in an ethylene matrix.

Temperature-programmed capillary chromatography was required to resolve and quantify such diverse analytes. Numerous capillary columns were housed in two patented, programmable, micro-convection ovens (MCOs) that wrap around the analytical columns to control temperatures precisely and rapidly. Packed columns were also used and housed in an isothermal oven. Electronic pressure and flow programming controlled the performance and resolving power of the analytical columns.

Column eluates were directed to three multiplexed detector trains (MSD, PDHID and FID). Combining the resolving power of capillary chromatography with the selective and discriminatory power of the MSD made GC-MS the best choice to address the oxygenates, sulfurs and metal hydrides. A proprietary mass spectrometer^b was used, and a proprietary PDHID^c was selected for the permanent gas analysis to achieve the low-ppb sensitivities requested.³ The common combination of a methanizer and an FID causes tailing of the CO and CO₂ peaks, which decreases the sensitivity for these analytes. PDHID does not suffer from this limitation. An FID is the best detector for hydrocarbon analysis and a proprietary FID^d was chosen for this application. The most common hydrocarbon impurities in monomer streams are hydrocarbons lighter than the monomer of interest. In the case of ethylene, methane and ethane are the most frequently observed contaminants. Heavier hydrocarbons were also potentially present and were characterized, as well.

This instrument used a single chromatographic method to control sample

acquisition and simultaneous analysis by the three detector trains. Unambiguous analyte detection and quantification were completed in < 10 min.

A custom sample conditioning system was designed to be mounted outside of the shelter and to accept eight sample streams: two ethylene streams and six calibration streams. Stream-selection valves delivered the chosen sample to sample-injection valves. Upon actuation, the injected sample was delivered, via a temperature-controlled bridge, to the analyzer inside the shelter (FIG. 4).

Once inside the analyzer, column-selection valves directed the sample to the appropriate analytical column for chromatographic separation and elution to the appropriate detector for identification and quantification. This design, with the sample system outside of the shelter and the analyzer inside the shelter, allowed for the bulk of the hazardous sample to be kept away from potential ignition sources inside the shelter. Only very small aliquots of sample gas (0.1 ml–1 ml each) were delivered to the Class 1, Division 2 hazardous area rated analyzer. Where appropriate, inert tubing and hardware were used to prevent analyte loss within the instrument.

Case study: Results. A 50-m capillary column in MCO2 resolved methanol, methyl mercaptan and ethyl mercaptan from a 10-ppm calibration blend (FIG. 5). The reference methods used were UOP 1015-17⁴, UOP 1021-19⁵, UOP 1022-18⁶, UOP 1023-18⁷ and UOP 1024-18⁸. Calculated minimal detectable limits (MDLs) were methanol (25 ppb), methyl

mercaptan (10 ppb) and ethyl mercaptan (15 ppb). Simultaneously, another capillary column in MCO2 resolved H₂S and COS. The MDL for COS was 10 ppb, while that for H₂S was 40 ppb. Arsine and phosphine (10 ppm each, as shown in FIG. 5) were also quantified with MDLs of 15 ppb and 30 ppb, respectively. Note that the retention times for many of these analytes are very similar; it would be difficult to resolve and quantitate them with another type of detector. However, the MSD's ability to generate an extracted ion chromatogram allowed for complete resolution and ppb level quantitation of these important compounds. The results of the process GC-MS system showed outstanding performance consistent with laboratory GC-MS systems.

At the same time, the PDHID train quantified CO, CO₂, hydrogen (H₂), O₂/argon (Ar) and nitrogen (N₂) from a 10-ppm calibration blend. The reference

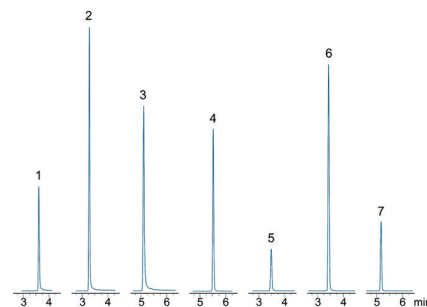


FIG. 5. Sulfurs, oxygenates and hydrides by MSD. Extracted ion chromatogram results for 1.) methanol with an m/z at 31; 2.) methyl mercaptan with an m/z at 47; 3.) ethyl mercaptan with an m/z at 62; 4.) carbonyl sulfide with an m/z at 60; 5.) hydrogen sulfide with an m/z at 34; 6.) arsine with an m/z at 76; and 7.) phosphine with an m/z at 34.

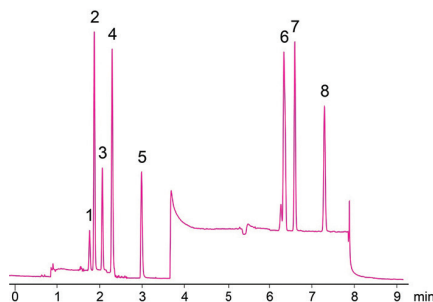


FIG. 6. Permanent gases by PDHID. Chromatogram of PDHID demonstrating 1.) hydrogen, 2.) oxygen/argon composite, 3.) nitrogen, 4.) methane*, 5.) carbon monoxide, 6.) hydrogen/air composite*, 7.) methane* and 8.) carbon dioxide. *Not quantified.



FIG. 4. Process GC monomer analyzer and sample system: (A) process gas chromatograph within the analyzer shelter; and (B) sample conditioning system mounted outside of the shelter, directly opposite the PGC. Samples are ported from the sample system to the analyzer through sample lines housed within a temperature-controlled heated bridge (black flexible tubing).

method used was ASTM D8098-17⁹. Two column sets in the isothermal oven, each with one packed and one capillary column, were used to separate the analytes (10 ppm each, as shown in FIG. 6). The chromatogram shows two sections with a rising baseline at 3.7 min resulting from the switch between the column sets. The first column set resolved and quantified H₂, O₂/Ar composite, N₂ and CO. The second column then set quantified CO₂. The observed baseline shift is a consequence of switching column sets during the run. The MDLs for these analytes were H₂ (100 ppb), O₂/Ar and N₂ (500 ppb), CO (20 ppb) and CO₂ (30 ppb). Methane was observed on each column set but analyzed by the FID (shown below).

While the MSD and PDHID trains were analyzing their respective compounds, the FID speciated and quantified hydrocarbons. The reference method used was ASTM D6159-17¹⁰. Here, an ethylene stream was interrogated for hydrocarbons (200-ppm refinery gas mix), which were resolved on a 50-m column in MCO1 and speciated by a flame ionization detector (FID, shown in FIG. 7). C₁–C₄ hydrocarbons were speciated while heavier species were backflushed as C₅₊.

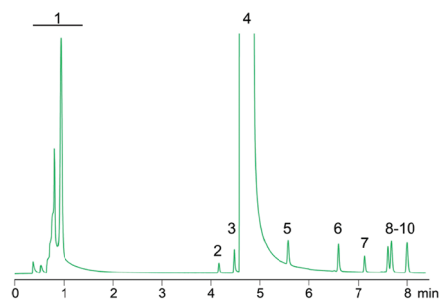


FIG. 7. Hydrocarbons by FID. Chromatogram showing results for 1.) C₅+ backflush, 2.) methane, 3.) ethane, 4.) ethylene*, 5.) propane, 6.) propylene, 7.) acetylene, 8.) propadiene, 9.) isobutane and 10.) n-butane. *Matrix.

A. Retention Times

	Methane	Pentane	Hexane	Heptane	Octane	Nonane	Decane	Undecane
Day 1	2.744	3.619	4.687	6.645	9.581	13.197	17.099	21.035
	2.775	3.653	4.723	6.683	9.613	13.225	17.118	21.038
	2.746	3.625	4.696	6.66	9.603	13.223	17.12	21.047
	2.747	3.626	4.697	6.663	9.604	13.223	17.118	21.049
	2.747	3.626	4.698	6.666	9.606	13.224	17.121	21.049
Day 2	2.747	3.625	4.694	6.659	9.598	13.213	17.108	21.036
	2.747	3.627	4.698	6.665	9.603	13.217	17.111	21.029
	2.745	3.624	4.694	6.662	9.601	13.215	17.106	21.033
Retention Time								
Avg.	2.750	3.628	4.698	6.663	9.601	13.217	17.113	21.040
StDev	0.010	0.010	0.011	0.010	0.009	0.009	0.008	0.008
RSD%	0.373	0.285	0.225	0.157	0.096	0.070	0.046	0.037

Data from 8 injections of hydrocarbon blend over 2 days.

B. Peak Areas

	Methane
Peak Areas	83767 83886
	84037 84020
	83813 83891
	83992 83966
	83727 83806
	83880 83859
Peak Area Avg.	
StDev	100.155
RSD%	0.119

Data from 12 injections of 5% methane in argon.

The MDL was determined to be 2 ppm for these components.

The precision of the micro-convection oven temperature and electronic pressure controls were also examined in a separate engineering study (FIG. 8). Retention time reproducibility is a measure of how tightly controlled the temperature, pressure and backpressure in a system are. To examine the retention time reproducibility, data taken over two days from eight injections of a hydrocarbon mixture were obtained. The relative standard deviation (%RSD) of the results was calculated and found to be excellent for all eight compounds in the blend. Peak area reproducibility is measure of a system's ability to repeatedly deliver the same amount of a sample to the analytical column. It is a function of split inlet performance and mass flow control. To evaluate these parameters, 5% methane in argon was injected 12 times. Again, %RSD results obtained rival those obtained on laboratory GCs and are unparalleled in online PGCs.

Takeaway. The goal of this study was to design a single PGC capable of ppb detection of analytes of importance for ethylene and propylene producers and their customers. A novel approach using process GC-MS was developed to take full advantage of the sensitivity and specificity of MSDs. Tightly controlled and temperature-programmable ovens allowed for the use of fused silica capillary columns for the greatest resolving power. Parallel chromatography with the MSD, PDHID and FID detector trains allowed for analysis of an extensive range of possible monomer contaminants at ppb levels not previously attainable with process GCs. Together, the data presented here clearly demonstrate that, when using the same technologies available to laboratory GCs, lab-quality performance can be achieved from a process instrument. **HP**

NOTES

- ^a Wasson-ECE Instrumentation's Eclipse Neutrin
- ^b Agilent Technologies' 5977B Mass Spectrometer
- ^c Valco PDHID
- ^d Wasson-ECE FID

REFERENCES

- ¹ Figure modified from the original, online: https://commons.wikimedia.org/wiki/File:Quadrupole_ion_trajectory.svg
- ² Silverstein, R. M., F. X. Webster and D. J. Kiemle, *Spectrometric identification of organic compounds*, 7th Ed., Wiley, 2005.
- ³ Wentworth, W. E., S. V. Vasin, S. D. Stearns and C. J. Meyer, "Pulsed discharge helium ionization detector," *Chromatographia*, Vol. 34, September/October 1992.
- ⁴ UOP Standard 1015-17, "Determination of trace oxygenates in polymer grade ethylene and propylene by gas chromatography mass spectrometry," Honeywell UOP, Des Plaines, Illinois, 2017, online: <https://www.astm.org/Standards/UOP1015.htm>
- ⁵ UOP Standard 1021-19, "Determination of trace methyl mercaptan, ethyl mercaptan, and isopropyl disulfide in polymer grade ethylene and propylene by gas chromatography mass spectrometry," Honeywell UOP, Des Plaines, Illinois, 2019, online: <https://www.astm.org/Standards/UOP1021.htm>
- ⁶ UOP Standard 1022-18, "Determination of trace carbonyl sulfide and hydrogen sulfide in polymer grade ethylene and propylene by gas chromatography mass spectrometry," Honeywell UOP, Des Plaines, Illinois, 2018, online: <https://www.astm.org/Standards/UOP1022.htm>

Complete Literature Cited available online at www.HydrocarbonProcessing.com



JOHN WASSON is the Founder and President of Wasson-ECE Instrumentation. Beginning with the industry's first gas autosampler in 1984 and continuing today with the industry's first process GC delivering lab-quality chromatography,

Mr. Wasson is a force for innovation in the field of gas chromatography. An MS degree in analytical chemistry from California Polytechnic Institute and early career training at Carle Instruments and Hach provided a strong foundation in GC fundamentals. Designing, building and applying more than 5,000 customized instruments has given Mr. Wasson a depth of expertise unparalleled in the specialty chemical and hydrocarbon processing industries. He built Wasson-ECE from a "start-up" in a garage to a multi-national company with offices in five countries.



A passion for analytical instrumentation and a wealth of troubleshooting and business skills make **THERESA RUSSELL** a valuable member of the Eclipse Process GC team at Wasson-ECE Instrumentation. Dr. Russell earned

a PhD in biochemistry from Colorado State University and has expertise in biomarker discovery using tandem mass spectrometry (MS/MS). As a patent-holding research scientist, she has contributed 14 peer-reviewed publications to the body of scientific knowledge in proteomics, infectious disease, cancer and diagnostic development. At Wasson-ECE, Dr. Russell contributes to the business side of science with technical writing, product management, business development and marketing.

FIG. 8. A screenshot of micro-convection oven performance.

ARCS for increased operational certainty in emergency shutdown situations

Emerson has released its ASCO™ 141 Series Advanced Redundant Control System (ARCS) to provide a redundant solution for a variety of emergency shutdown valve applications, such as those found in the chemical, power, oil and gas industries. Available globally, the system (FIG. 1) includes various redundant solenoid configurations to enhance the reliability of the process and meet specific safety or reliability requirements in automation processes. The single-inlet/single-outlet design provides a streamlined installation process compared to traditional bypass systems, while almost eliminating potential failure points.

The ASCO 141 series ARCS is designed for use as a component in safety instrumented systems. Utilizing 1oo2, 2oo2 or 2oo3 voting solenoids to enhance the reliability of the circuit, it functions as a redundant pneumatics tripping device to control the pilot air signal to a process valve actuator. The ARCS features either two or four electrically actuated solenoid valves, visual indicators and a manually controlled bypass or isolation valve. The unique control functionality allows for maintenance of the solenoid valves without having to shut down the process valve. In fact, the use of the maintenance bypass or isolation valve is not required for functional testing of the ARCS unit—a downtime-reducing feature not possible with common bypass functions.

With just a single part number, the ASCO 141 series ARCS features several advances that simplify specification, installation and operation. Supplied as a fully integrated, comprehensive solution using a manifold instead of individual valves, ARCS comes pre-tested from the factory and ready to install. The direct valve-to-valve design eliminates pipework and fittings between the solenoid valves and minimizes leak points for increased reliability

and a lower total cost of ownership. A status indicator with feedback helps facilitate preventive maintenance while providing online fault detection. It provides digital input feedback (via pressure switches or Emerson-exclusive GO Switch options) to the control room. For additional peace of mind, the ASCO™ 327 series 3/2-way direct acting solenoid valves included on the ARCS manifold are certified to SIL 3 capable (exida) standards.

Natural gas analyzer

SpectraSensors, an Endress+Hauser company, has released its J22 TDLAS gas analyzer. This new product addresses multiple issues with traditional technologies used for the measurement of moisture content in natural gas, while providing additional benefits.

Gas suppliers, pipeline operators and industrial users must accommodate unexpected changes in heating value and contaminant levels by using analyzers to verify characteristics throughout the supply chain. One critical contaminant must be monitored continuously: H₂O. The presence of water content in liquid or gas can cause corrosion in a pipeline or other assets. Moisture and other acids can combine to cause severe asset degradation.

The J22 moisture analyzer (FIG. 2) combines Endress+Hauser's and SpectraSensors' more than two decades of experience producing tunable diode laser analyzers with the latest advancements in data analysis, internal diagnostics, multi-functional enclosures and web server connectivity. The combination of these features creates a comprehensive moisture monitoring solution with unique capabilities.

The analyzer can replace traditional electrochemical sensors, such as aluminum oxide, phosphorus pentoxide, quartz crystal microbalance and chilled mirror. These technologies often lose accuracy due to contamination issues, require frequent maintenance and cannot reliably distinguish between water and other liquids frequently found in gas streams, such as glycol and methanol.

TDLAS technology can identify the water molecules specifically, while being unaffected by a wide variety of other common contaminants. However, some traditional TDLAS analyzers are difficult to maintain and not suited to installation in harsh environments.

To address these and other issues, the J22 TDLAS gas analyzer is designed for almost zero maintenance. When service is required, its components are easily accessible and field-serviceable, allowing for quick replacements and upgrades. The gas sample cell is simple to remove and designed for convenient cleaning and servicing. The available IP66 and Type 4X enclosures for housing the analyzer system are suitable for installation in typical natural gas application locations.

Field operability is made easier thanks to Endress+Hauser's Heartbeat Technolo-

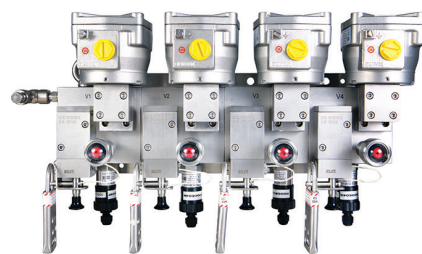


FIG. 1. Emerson's ASCO™ 141 Series Advanced Redundant Control System (ARCS).

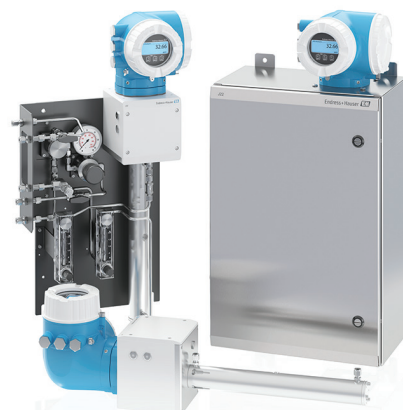


FIG. 2. SpectraSensors, an Endress+Hauser company, has released its J22 TDLAS gas analyzer.

gy™, with diagnostic capabilities built into the J22 TDLAS gas analyzer. Alerts and verification reports advise operators on how the unit is performing and will inform the operator if the health of the analyzer is degrading. When severe enough, the system triggers alarms to call for maintenance attention. Operators can quickly interpret alerts, thanks to NAMUR 107 compliant alarm categories and diagnostic graphics.

The analyzer has a built-in web server, with connectivity provided to a laptop or other device via an Ethernet cable. This functionality allows operators to find further detail through information screens and verification reports, the latter provided in PDF format.

Measure density of condensate

The Dynatrol® Density System (FIG. 3) consists of two components: the CL10-HYv2 density cell and a Series 2000 digital converter to measure the density of condensate.

Dynatrol density cells achieve exceptional accuracy and are rugged enough to withstand harsh environments. The density cells come in a full range of corrosion-resistant materials that are both weather-tight and explosion proof. They also serve broad temperature and pressure ratings.

The Dynatrol CL10HY-V2 cell is double-sealed for protection against

leaks and provides density measurement for high-pressure service up to 1,480 psig. There are no motors, bearings, spindles or moving parts to maintain, which provides and ensures a virtually wear-free and long operating life.

The 2000 Density Digital Converter calculates specific gravity, API gravity and can also display corrected gravities using information generated from the density cell. It incorporates an onboard microcontroller, is precalibrated and ready for use. A two-line LCD displays temperature, density, product frequency and status. The converter has a 4-20MA standard output and a RS-232 two-way communication.

SPONSORED PRODUCT RELEASE

Achieve maximum SO_x emissions control



Refiners around the world have adapted to meet stringent sulfur oxide (SO_x) emissions limits over the past few decades. In some regions of the world, these emissions limits are newly imposed. SO_x reduction additives have long been established in fluid catalytic cracking units (FCCUs) as a reliable and cost-effective technology solution to help refineries remain in SO_x emissions compliance. New advances in SO_x reduction additives made by W. R. Grace & Co. provide refiners with an opportunity to maintain compliance with lower operating expenses. This is being achieved directly through reduced SO_x additive usage rates or caustic consumption in wet gas scrubbing.

Grace is a unique supplier of SO_x reduction additives, with a full commitment to continued investment in FCC SO_x reduction technologies. This is demonstrated by the commercialization of EMISSCIAN® additive, a new FCC SO_x reduction additive providing step out performance. EMISSCIAN additive is based on Grace's renowned DESOX® technology platform and is the result of a significant capital investment

made at its SO_x additive manufacturing facilities, where an additional processing step was incorporated to improve the physical properties of the additive. Compared to the previous Super DESOX® additive, the new EMISSCIAN additive boasts improved cerium and vanadium dispersion across the additive particle, as well as increased magnesium aluminate spinel content, both of which bring significant improvement in SO_x reduction performance.

More than 20 refiners worldwide have successfully switched from alternative technologies to EMISSCIAN technology. The additive has been demonstrated to be very effective in both partial and full-burn applications. This is demonstrated by the article in the September issue of *Hydrocarbon Processing*, which describes the successful switch from competitor SO_x additive technology at the BP Rotterdam refinery, which is a full-burn application. This refinery first switched to the company's Super DESOX additive, and then to its latest EMISSCIAN additive with performance improvements observed in both stages. Grace is also preparing an upcoming article, where the company will openly co-publish with a national oil company a case study describing the successful switch from a competitor's partial-burn SO_x additive to EMISSCIAN technology, resulting in improved SO_x reduction performance.

EMISSCIAN additives' commercial success in a variety of applications paved the way to the next generation SO_x additive that can be successfully applied for all types of operating conditions, including partial burn and low reactor severity. This allows refineries to be confident in SO_x additive performance, regardless of shifting operational modes at the FCCU. EMISSCIAN additive has proven to be considerably more cost-effective than the use of alternative SO_x additives that are typically positioned specifically for certain applications.

Converting 100% of naphtha into cleaner-burning Euro 5 gasoline

Honeywell UOP has developed a new refinery configuration to produce a cleaner-burning gasoline product that meets increasingly stringent fuel regulations.

The UOP Premium Gasoline Complex (PGC) employs a combination of technologies to convert 100% of naphtha into 95 RON (research octane number) Euro 5 gasoline—without the addition of traditional octane boosters such as alkylate, MTBE, ETBE and ethanol—to meet these specifications, such as aromatics, olefins and Reid Vapor Pressure.

The PGC configuration operates through four main processes, beginning with full-range naphtha that is fed to a naphtha hydrotreating unit, and a naphtha splitter separates the product into an overhead stream of C_5/C_6 components. From there, the product moves to a Penex™ unit, then to a sidecut stream primarily of C_7 s to an IsomEx™ isomerization unit, and finally to a bottom stream rich in C_8+ com-

ponents to a CCR Platforming™ unit.

UOP's IsomEx technology can also be employed to increase the capacity of existing Platforming units by separately processing C_7 s that would otherwise be fed to a Platforming unit. The addition of an IsomEx unit, in effect, can expand the processing capacity of a Platforming unit by as much as 20%.

UOP is a leading global provider of each technology within the UOP Premium Gasoline Complex. More than 350 light naphtha isomerization units are in operation or in design and construction. The CCR Platforming process produces reformat for high-octane, low-sulfur gasoline and aromatics, and is designed as a reliable, continuous source of high-purity hydrogen for the production of other fuel products. Since it was first introduced in 1971, more than 375 CCR Platforming units are in operation or in design and construction worldwide.

The Penex process upgrades light naphtha feedstock to produce isomerate, a cleaner gasoline blend stock that does not contain benzene, aromatics or olefins.

The new IsomEx technology isomerizes the C_7 components, helping to maximize the C_7 contribution to the gasoline pool, while maintaining high yield and limiting production of aromatics.

The conventional feed for the complex is full range straight run naphtha from a crude unit. Depending on the refinery configuration, upstream conversion unit and the gasoline pool requirements, other naphtha such as hydrocracked naphtha can be processed within the UOP Premium Gasoline Complex to help ensure maximum production of premium gasoline. **HP**



FIG. 3. The Dynatrol® Density System consists of two components: the CL10-HYv2 density cell and a Series 2000 digital converter.

Optimizing operations and maintenance in the HPI

September 21–22

- Preconference Innovation Showcase sponsored by Axens
- Nearly 50 technical presentations
- Live virtual Q&A with presenters
- Free to attend

www.IRPC-Operations.com

The hydrocarbon processing industry (HPI) is constantly investing in new technologies to optimize operations. These initiatives are aimed at providing refiners and petrochemical producers with the technologies and services for safer, more reliable, more profitable and sustainable operations. These technologies and services will be on display at *Hydrocarbon Processing's* IRPC Operations technical event.

Built after a successful IRPC Process Technology event, which garnered more than 1,600 registrants worldwide, IRPC Operations will be held virtually September 21–22. This global, virtual event will feature three tracks that focus on optimizing refining and petrochemical plant operations. Nearly 70% of the event's presentations will be led by owner-operator organizations from nearly 20 countries around the world.

Innovations Showcase. Prior to the start of IRPC Operations, a one-day seminar will be held by Axens. The Innovation Showcase workshop will provide viewers the latest Axens technologies that are revolutionizing the refining and

petrochemical industries. The workshop will be followed by the two-day IRPC Operations virtual event.

Keynote presentations. IRPC Operations' keynote presentations will provide viewers the latest technologies and project information on key themes affecting the HPI, such as carbon capture, the increase production of petrochemicals and using the available tools (e.g., digital technologies) to increase reliability and operational excellence. These keynote presentations include:

- **Decarbonizing Shell Pernis: Porthos CCS and other projects:** Andy Goose, *President*, Shell Catalysts and Technologies
- **A critical analysis on CO₂ capture technologies:** Ajay Jha, *Senior Scientist, Refining R&D*, Reliance Industries Ltd.
- **Tools to increase operational awareness and reliability:** Walter Pesenti, *Global Operational Excellence Manager*, INEOS Aromatics
- **The future of petrochemicals: An outlook:** Dr. Thomas Kevin Smith, *Chief Economist and Managing Director*, American Chemistry Council.

The keynote presentations will be followed by tracks on the following topics: alternative fuels, biofuels and clean fuels; catalysts; digital transformation; engineering and construction; environment and safety; maintenance and reliability; process controls, instrumentation and automation; process optimization; refining-petrochemical integration; valves, pumps and turbomachinery; and water management.

These sessions will be feature technologies, case studies and best practices

by companies such as Axens, Babcock and Wilcox, BASF, Bharat Petroleum Corp. Ltd., Chevron, Citgo, Clariant, CNOOC Ltd., COOEC Canada Co. Ltd., Covestro, Eastman Chemical, Dynamics Scientific Production Center USA, ENAP, Engro Fertilizers, Exxon-Mobil, Fluor, Honeywell UOP, Hytech, Indian Oil Corp. Ltd., Indorama Petrochemicals, Kuwait National Petroleum Co., Kuwait Oil Co., Linde, Methanex, Pentair, Petrobras, PetroChina Co. Ltd., Petrofac, Petronas, Raffineria di Milazzo, Reliance Industries Ltd., Saudi Aramco, SCG Chemicals, Schlumberger, SK Energy, SUEZ Water Technologies and Solutions, Suncor, Technip Energies and Tupras.

Additional benefits of attending *Hydrocarbon Processing's* IRPC Operations digital event include:

- No cost—IRPC Process Technology is free to register and attend
- No travel—All presentations can be viewed from anywhere with an internet connection
- Engaged participation—An enhanced chat function enables viewers the ability to speak and ask questions of various presenters
- Enhanced archives—Registrants can access event presentations, whitepapers, marketing collateral, etc., for one year
- Networking—The digital platform contains an enhanced virtual networking system to enable attendees to “meet” and chat with speakers and other attendees.

IRPC Operations is a free online event; however, you must register to attend. To register, access the agenda or view sponsorship opportunities, visit www.IRPC-Operations.com. **HP**